
# SYNTHESIS AND CHARACTERIZATION OF MACROCYCLIC COMPLEXES CONTAINING N, O or S AS BITING CENTERS

## ABSTRACT

**THESIS**

SUBMITTED FOR THE AWARD OF THE DEGREE OF

**Doctor of Philosophy**

IN

**CHEMISTRY**

BY

**SHAKIRA KHATOON**

DEPARTMENT OF CHEMISTRY
ALIGARH MUSLIM UNIVERSITY
ALIGARH (INDIA)

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# ABSTRACT

The chemistry of macrocyclic compounds has been an interesting and fascinating area of research activity during last few decades. It lies at the centre of organic and inorganic chemistry and became the basis for development of bioinorganic chemistry. The continued efforts of chemists to proliferate this chemistry are not only due to structural novelties of these compounds but also because of their varied applications. Therefore, the work embodied in the Ph.D thesis aims the synthesis and physico-chemical studies of macrocyclic moieties containing N, O or S as donor atoms and their complexes with first row transition metal ions Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) via organic and template procedures showing new structural features. Some of the complexes were analyzed for antimicrobial activities. The whole work is divided into five chapters.

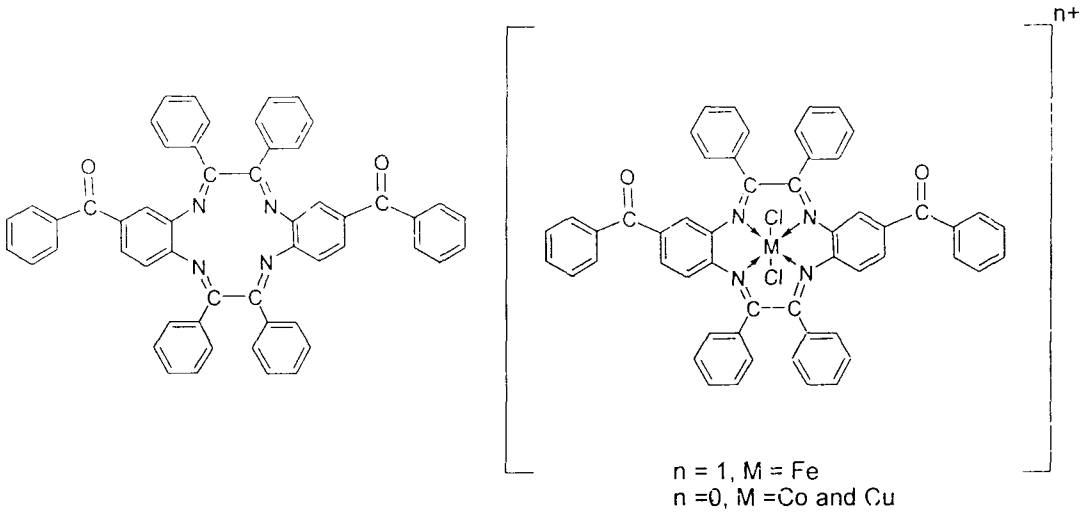
**Chapter 1** deals with the comprehensive account of work carried out on several classes of macrocycles, general characteristics, different types of synthetic procedures, potential applications and the pioneering work extracted from different reviews, articles and hundreds of research publications reported by various eminent chemists through out the world during past few decades.

**Chapter 2** gives the detailed account of physico-chemical methods, the instruments and the experimental conditions involved to ascertain the

stoichiometry, nature and molecular geometry of the newly synthesized macrocyclic moieties viz; IR, NMR, EPR, UV-vis, Magnetic Susceptibility, Molar Conductance, FAB-mass, Elemental analyses and Job's method.

**Chapter 3** explains the synthesis and spectral characterization of 12-membered tetraimine macrocyclic ligand, (L): **5,6;11,12-dibenzophenone-2,3;8,9-tetraphenyl-1,4,7,10-tetraazacyclo-dodeca-1,3,7,9-tetraene,** derived from the [2+2] condensation of 3,4-diaminobenzophenone and benzil in a 1:1 molar ratio in methanol at room temperature. The macrocyclic complexes of the type, $[FeLCl_2]Cl$ and $[MLCl_2]$ [M = Co(II) and Cu(II)] have been prepared by reacting iron(III) chloride or metal(II) chlorides with the ligand, (L) in 1:1 molar ratio in methanol. The stoichiometry corresponding to the formation of the ligand framework, was ascertained on the basis of results of elemental analyses, $^1$H-NMR and FAB-mass measurements while that of complexes were also ascertained by results of elemental analyses and in solution by Job's method. The Job diagrams obtained for iron(III), cobalt(II) and copper(II) complexes at $\lambda$= 490, 500 and 645 nm respectively, intersect at $X$ = 0.5, suggesting 1:1 stoichiometry of each complex. The mode of bonding and the geometry of the complexes have been confirmed on the basis of IR, UV-vis spectral findings and magnetic susceptibility measurements which revealed an octahedral geometry for all the complexes. The IR spectrum showed the

appearance of the ν(C=N) band at 1625 $cm^{-1}$ indicating that Schiff base condensation between carbonyl groups of benzil and amino groups of 3,4-diaminobenzophenone has taken place. A significant negative shift in ν(C=N) stretching mode appearing in 1580–1560 $cm^{-1}$ region for the complexes as compared to free ligand suggests the involvement of imine nitrogens of the (C=N) groups in coordination with metal ions. $^1$H-NMR spectrum of the ligand shows signals in the range of 7.31-8.32 ppm indicating the presence of ring protons. The nature of the complexes was confirmed by conductometric studies.

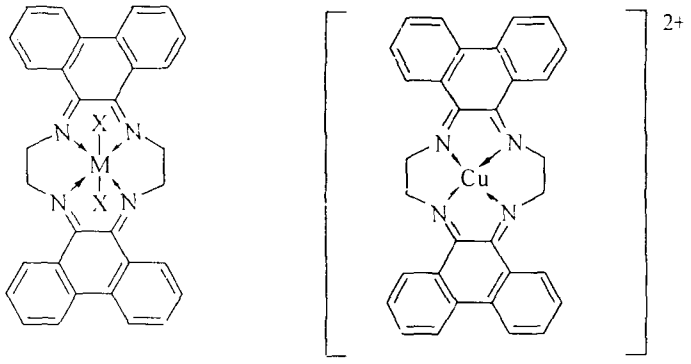



Suggested structure of the ligand and the macrocyclic complexes

**Chapter 4** describes the synthesis and pysico-chemical studies of the tetraazamacrocyclic complexes: **dichloro/dinitrato(2,3;8,9-diphenantherene-1,4,7,10-tetraiminecyclododecane) metal(II) [$MLX_2$]; (M = Mn(II), Fe(II), Co(II), Ni(II) and Zn(II); X = Cl and $NO_3$)** and **(2,3;8,9-diphenantherene-**

**1,4,7,10-tetraimine-cyclododecane) Copper(II)chloride or nitrate $[CuL]X_2$ (X= Cl and $NO_3$).** The synthesis of these macrocyclic moieties have been accomplished by the template condensation of 9,10-phenanthrenequinone and 1,2-diaminoethane in 2:2:1 molar ratio. The composition of these macrocyclic complexes have been ascertained on the basis of elemental analyses, resonance signals obtained on recording $^{1}$H- and $^{13}$C-NMR spectra. The chemical shift ($\delta$) values in 9.16-9.07 ppm (Ar- 8H, m), 8.80-7.87 ppm (Ar- 8H, m), regions may reasonably be assigned to phenantherene ring protons and 2.40-2.35 ppm (8H, s) region corresponds to methylene protons of condensed 1,2-diaminoethane moiety. The decoupled $^{13}$C-NMR spectra of the Zn(II) complexes at room temperature also confirm the presence of imine, methylene and aromatic functions in the macrocyclic complexes. The mode of bonding and the geometry of the complexes have been ascertained on the basis of band positions observed in IR and Uv-vis spectra, the values of $g_{\|}$ and $g_{\perp}$ in the EPR spectra of Cu(II) complexes and magnetic moment data. These studies revealed an octahedral geometry for all the complexes except the Cu(II) complexes, which have square planar arrangement. The non-ionic nature of Mn(II), Fe(II), Co(II) Ni(II) and Zn(II) and ionic nature of the Cu(II) complexes were ascertained on the basis of conductometric studies. The antimicrobial screening test were also

recorded for Fe(II), Ni(II) and Cu(II) complexes, which revealed maximum inhibition by Cu(II) complex as compared to Fe(II) and Ni(II) complexes.

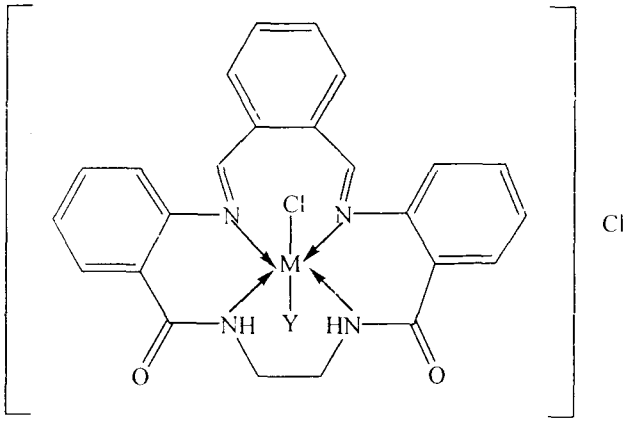



$[MLX_2]$ $[CuL]X_2$

Proposed structure of the macrocyclic complexes

**Chapter 5** deals with the synthesis and spectral characterization of 16-membered diamidediimine tetraazamacrocyclic Complexes: **chloro(1,2:5,6: 9,10-triphenyl-11,16-dioxo-3,8,12,15-tetraazacyclohexadeca-3,7-diene)metal (II)chloride, [MLCl]Cl [M= Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)].** These complexes have been prepared by the metal-promoted reaction between o-aminobenzoic acid, phthalaldehyde and 1,2-diaminoethane in 1:2:1:1 molar ratio. The results of elemental analysis and conductivity data confirm the proposed stoichiometry of the complexes. The formation of macrocyclic framework has been deduced on the basis of characteristic IR and Proton resonance peaks of various functional groups of the complexes viz. coordinated

ν(C=N), ν(N-H), amide I [ν(C=O)], amide II [ν(C-N) + δ(N-H)], amide III [δ(N-H)] and amide IV [ϕ(C=O)] vibrations, etc in the Ir spectra and amide, methylene, imine and phenylene ring proton resonance signals of condensed o-aminobenzoic acid, o-phthalaldehyde and 1,2-diaminoethane from Proton NMR spectra, respectively. The overall geometry of the complexes was ascertained on assignments of absorption bands in UV-Vis and bands in reflectance spectra. A pseudo-octahedral geometry has been suggested for all complexes in DMSO, while a pentacoordination environment has been noticed around the metal ion in the reflectance spectra of Fe (II), Co (II), Ni (II) and Cu (II) complexes.




Suggested structure of the macrocyclic complexes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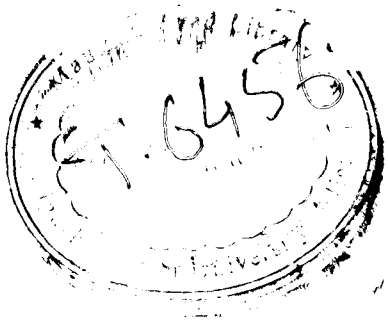





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# Certificate

Certified that the work embodied in this thesis entitled **"Synthesis and characterization of macrocyclic complexes containing N, O or S as biting centers"** is the result of original researches carried out by **Ms. Shakira Khatoon** under my supervision and is suitable for submission for the award of the Ph.D. degree of Aligarh Muslim University, Aligarh, India.

**(Prof. Mohammad Shakir)**

*DEDICATED*

*TO*

*MY PARENTS*

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*At last I am fumbling for words to express my feelings for my family. My present status in life is the result of the extraordinary will, efforts and sacrifices made by my parents Mr. Khalid Ahmad and Mrs. Basharat Sultana. The blessings of my parents have always made up my enthusiasm throughout the sturdy times. It is indeed a privilege to bring up the name of my sister Mrs. Rafia and my brother-in-law Mr. Majid Bashir Malik for their unrelenting support and kind concern.*

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Shakira Khatoon

*(SHAKIRA KHATOON)*

# CONTENTS

# LIST OF PUBLICATIONS

- Synthesis and spectral studies of 12-membered tetraimine macrocyclic ligand and its complexes
  *Transition Met. Chem.*, 2007, **32**, 42-46.

- Metal-ion directed synthesis and characterization of tetraimine macrocyclic complexes derived from 9,10-phenanthrenequinone and 1,2-diaminoethane.
  *Transition Met. Chem.*, 2007, (Communicated)

- Synthesis and spectral studies on 16-membered diamidediimine tetraazamacrocyclic complexes, [MLCl]Cl [M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)].
  *Polish J. Chem.*, 2005, **79**, 1627-1633.

# CHAPTER-1

# Review of Literature

# 1.1 INTRODUCTION

Coordination chemistry of macrocyclic ligands has become a growing field of research owing to the recognition of their active role played in the fields of chemistry and biochemistry. Historically the concept of coordination chemistry was associated with the complexation of metal cation (Lewis acid) by a ligand (Lewis base). The chemists all over the world are busy in exploring the coordination chemistry of macrocycles, porphyrins and related systems so as to mimic them for their benefits. This has led to the development of a new field of coordination chemistry known as macrocyclic chemistry. A macrocycle, is as defined by IUPAC, "A cyclic macromolecule". Generally however, when speaking of a macrocycle, coordination chemists define macrocycle as a cyclic compound having nine or more heteroatomic members and with three or more ligating groups[1]. The enormous amount of work carried out by countless researchers with their contribution towards thousands of research papers, hundred of reviews and numerous patents make the basis for the development of coordination chemistry of the macrocyclic ligands and it is almost impossible to confine their work in this introduction. However, prior to 19$^{th}$ century their existed only well established category of synthetic macrocyclic ligands containing nitrogen atoms, which were the highly conjugated phthalocyanines. The phthalocyanines **Figure 1** and its

derivatives bear a strong structural resemblance to the biologically important compounds such as the green pigment of chlorophyll and the heame of hemoglobin. These biologically important compounds were known as tetrapyrrole macrocycles. In 1886, Baeyer[2] synthesized the first reported macrocycle possessing a pyrrole heterocyclic ring **Figure 2**, resembling the porphyrins, via an acid catalyzed condensation between pyrrole and acetone.

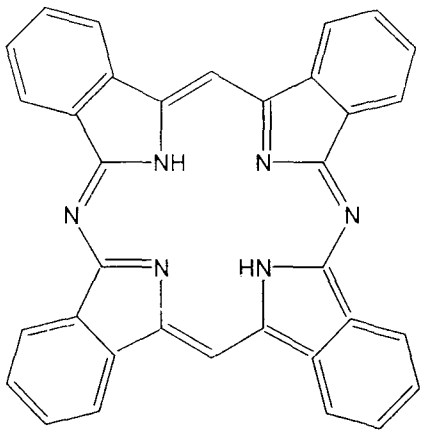



**Figure 1**

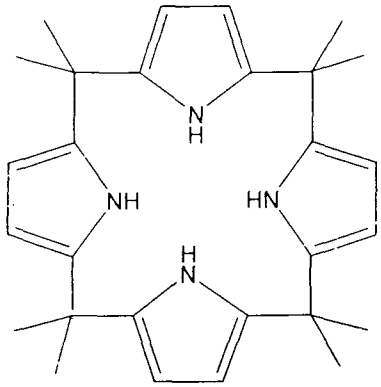



**Figure 2**

The early part of 1930's saw significant interest in complexed nitrogen containing macrocycles (azacrowns) because of their industrial importance as pigments and dyeing agents. It is also interesting to note that in 1937, the same year that Luttringhaus[3] synthesized the first cyclic polyether **Figure 3**, Alphen obtained the first saturated macrocycle polyamine, cyclam **Figure 4**.

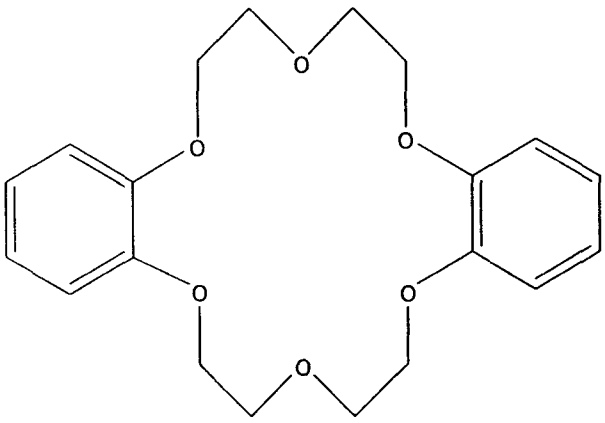



**Figure 3**

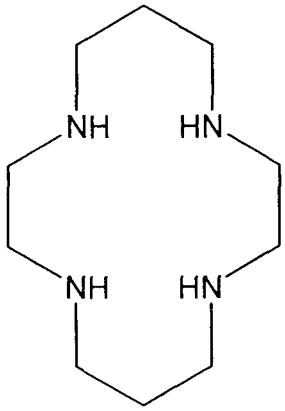
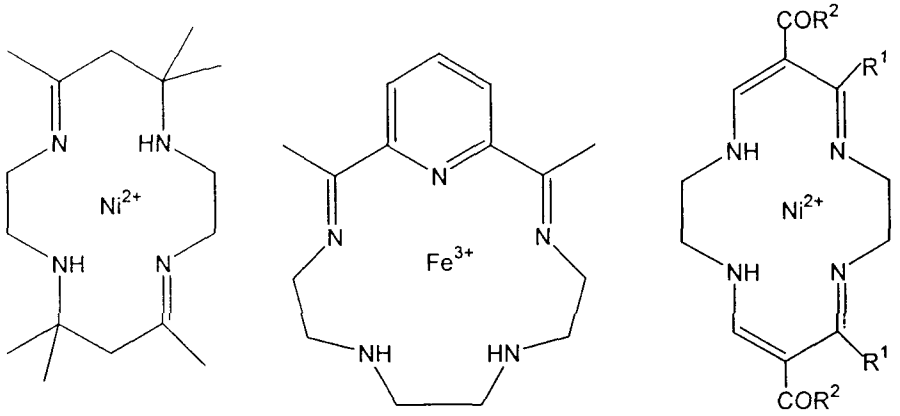



**Figure 4**

Since then, lot of advances have taken place considerably in the late 60's and early 70's in the field of coordination chemistry of polyazamacrocycles by the pioneering and independent contributions of eminent scientists like Curtis[4], Busch[5], Jager and Pedersen **Figure 5**. Charles J. Pedersen's publication[6] in 1967, "synthesis and characterization of over 30 new cyclic polyether macrocycles" initiated tremendous and continuing interest in scientific community. This interest was stimulated by the possibility of molecular recognition in new ways by the macrocycles, which led the coordination chemists to more systematic studies and as such provided the basic platform on which the supramolecular chemistry has been built.



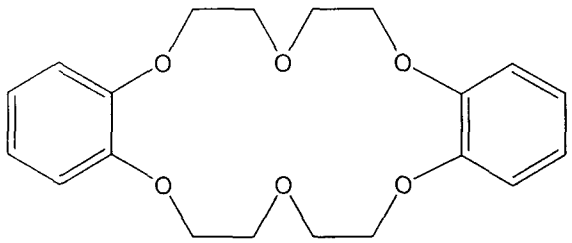




**Figure 5**. The cornerstone macrocycles

Macrocyclic compounds display unique and exciting chemistry because they offer a wide variety of donor atoms, ionic charges, coordination numbers and geometries of the resultant complexes[7-10]. It would not be a total exaggeration to state that macrocyclic ligand lie at the centre of life, particularly with regard to the roles of such systems in understanding and explaining the mechanism of photosynthesis[11], transport of oxygen in mammalian and other respiratory systems and in the potency towards DNA binders with a high potential in anti-tumor therapy[12,13]. Apart from the biological implications, macrocyclic

chemistry plays a dynamic role in the other areas, where these macrocyclic ligands act as model to study magnetic exchange phenomena[14], as sensitizer for photodynamic therapy[15,16] (PDT) in cancers, as therapeutic reagents[17], in chelate therapy for the treatment of metal intoxication, as synthetic ionophores[18,19], as novel antibiotics that owe their antibiotic actions to specific metal complexation[20,21], as efficient contrast agents for magnetic resonance imaging (MRI)[22,23]. The macrocycles have also been used for the treatment of AIDS, stem cell mobilization[24], to study the host guest interaction and in catalysis[19,25,26], as metal extractants[27] and as luminescent probes. Macrocyclic molecules can also function as receptors for substrates of widely differing physical and chemical properties, which can be drastically altered upon complexation.

Strategies to the architectural design involve the knowledge of the metal ion binding preferences and its efficient utilization in the synthesis of macrocyclic ligands by introducing site and geometry control. Several classes of macrocyclic ligands have been synthesized with varying combination of aza (N), oxa (O), sulpha (S) and phospha (P) donor atoms. Interaction between the macrocyclic ligand and the substrates can be fine-tuned by appropriate selection of the binding site, and overall ligand topology such as nature of

donor atoms, donor set, donor array, ligand substitution and nature of ligand backbone. Other factors considered are as under:

a. Electronic effects- such as charge, polarity and polarizability of the binding sites are the major influences in the complex stability[28].
b. Structural effects- this aspect is very crucial for selective complexation of a substrate by a macrocyclic ligand. Hence, in general, the number of binding sites should be at least equal to the coordination number of the cation.
c. Conformation- complexation can be complicated by the existence of more than one conformation for a given macrocyclic ligand. Greater complex stability is achieved when the built in conformations in the free ligand and complexed ligand are same.
d. Shaping groups- the nature and as a consequence the selectivity of a particular macrocycle can be further manipulated by the selection of appropriate shaping groups and heteroatoms on the binding sites. In general saturated chains provide greater flexibility and total macrocyclic ring size is increased. However, unsaturation results in the steric constraints on the molecule as a result of which flexibility is at a minimum[28].

e. Cavity size- the number of the donor atoms in the macrocycle and the imposed degree of rigidity influence the nature of the cavity. While a rigid framework results in a preformed cavity, flexibility allows latent cavity formation.

The extensive series of macrocyclic ligands, which have been synthesized in the last 2-3 decades, have been classified into various sub-divisions[29] **Figure 6 (I-XV)**.

i. Coronads[30,31] **(I)** and **(II)** are macrocyclic species which contain various heteroatoms as binding sites. The complexes of these ligands are referred to as coronates.

ii. Crown ethers[32] **(III)** and **(IV)** are macrocyclic polyethers.

iii. Podands[33] **(V)** are acyclic host with pendant binding sites.

iv. Lariat ethers[34] **(VI)** are crown ethers or similar macrocycles with appendages or pendants.

v. Spherands[35] **(VII)** and hemispherands[36] **(VIII)** are rigid hosts which consist of arrangement of phenyl groups and have the donor atoms forced to converge on central site.

vi. Calixarenes[37] **(IX)** are macrocyclic phenol-formaldehyde condensation products.

vii. Catapinands[38] **(X)** are diazabicycloalkanes.

viii. Catenands[39] **(XI)** are two separate, but interlocked macrocycles.

ix. Cryptands[40] **(XII)** are the macropolycyclic receptor molecules, which provide a cavity for inclusion of a variety of substrates.

x. Cyclidenes[41] **(XIII)** are bicyclic macrocycles, which coordinate one metal ion and contain a protected "void" about the axial site of the metal ion.

xi. Sepulchrates[42] **(XIV)** are polyaza macrobicycles analogous to the cryptands.

xii. Speleands[43] **(XV)** are hollow, macropolycyclic molecules formed by the combination of polar binding units with rigid shaping groups.

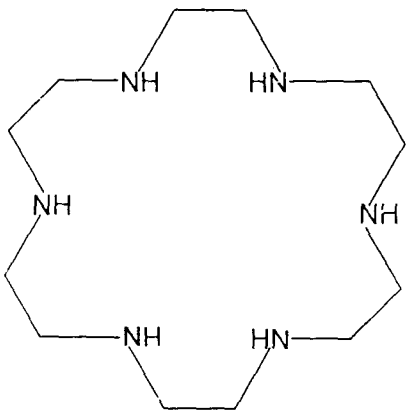



Figure 6 - (I)

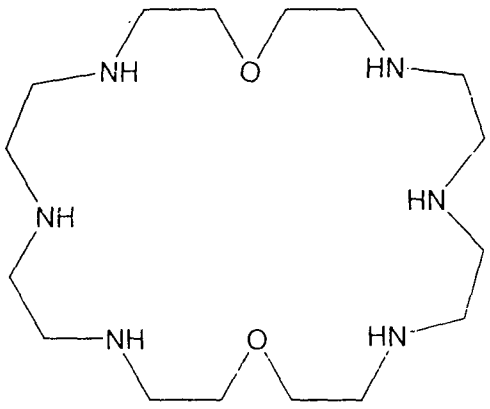
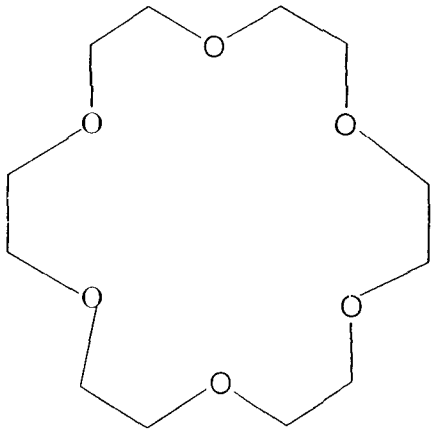



Figure 6 - (II)



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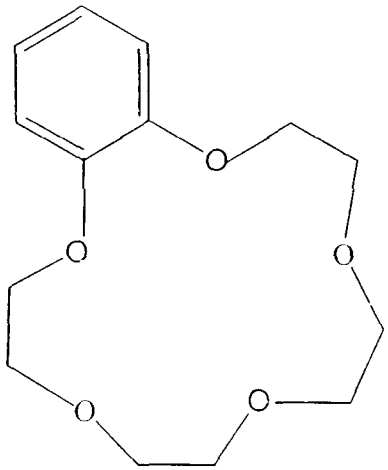

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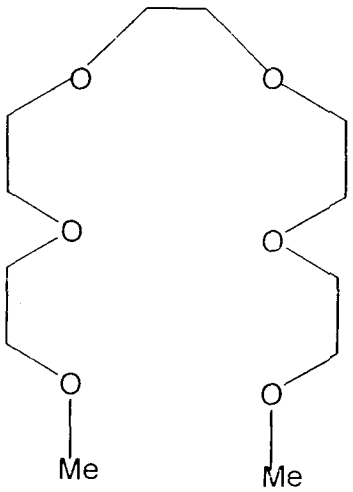


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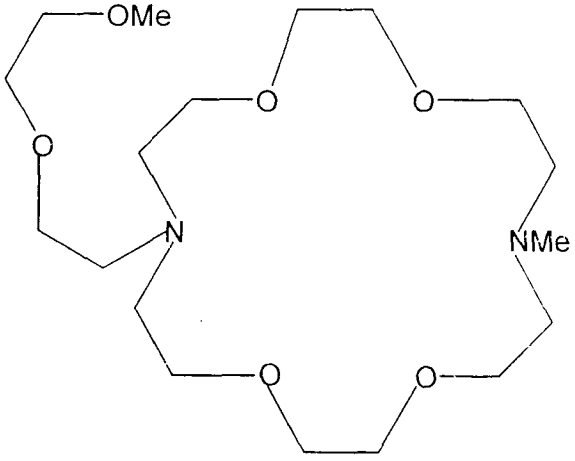



Figure 6 - (VI)

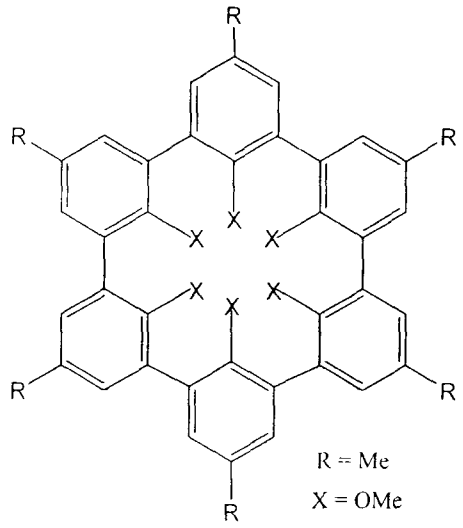



Figure 6 - (VII)

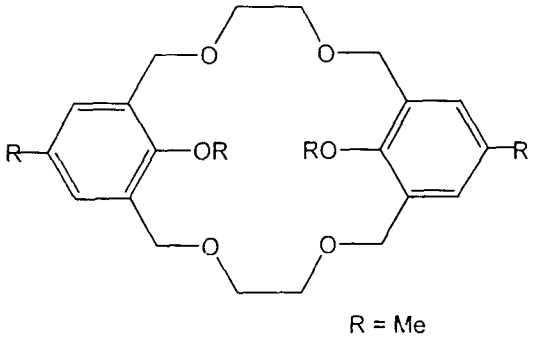



Figure 6 - (VIII)

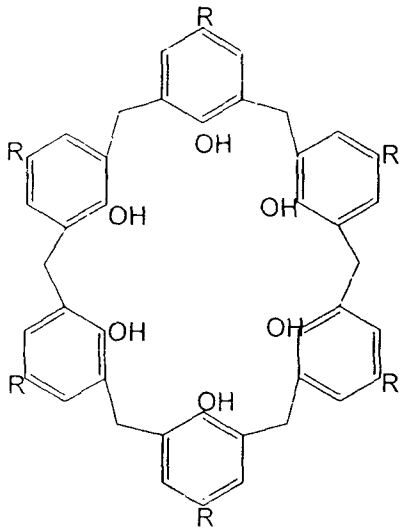



Figure 6 - (IX)

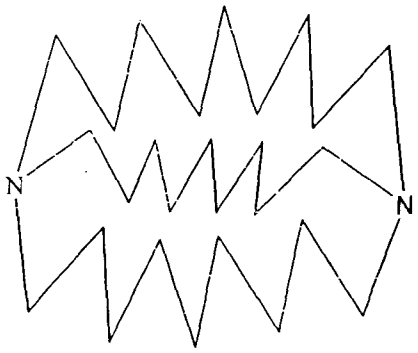



Figure 6 - (X)

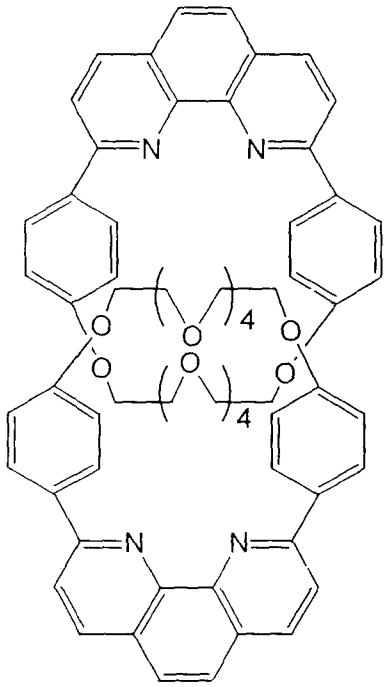



Figure 6 - (XI)

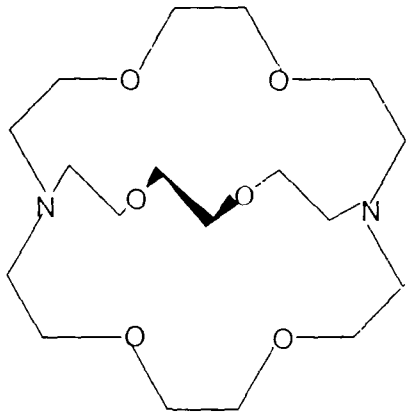



Figure 6 - (XII)

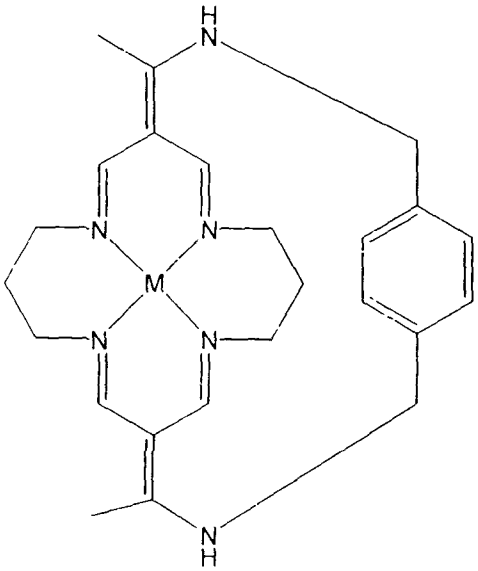



Figure 6 - (XIII)

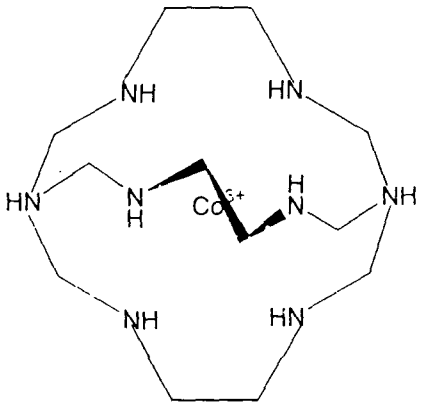



Figure 6 - (XIV)

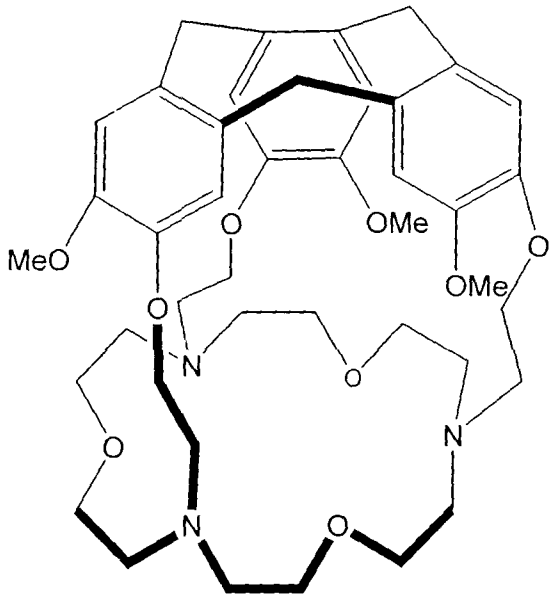



**Figure 6-(XV)**

The compounds shown in **Figure 6 (I-XV)** differ in type and number of ion binding sites and thus generally exhibit quite different affinities for a given metal ion.

Macrocycles are important and potential ligands, ubiquitous in transition metal coordination chemistry as they impart thermodynamic and kinetic stabilities to their metal complexes[44,45]. Macrocyclic ligands are far more stable as compared to their open chain analogues as they have stereochemical constraints associated with their cyclic nature, which may influence their potential for metal-ion recognition[46]. The several ligands coordinated to a

metal ion are held in specific geometric orientations and recognition of this fact led to the "coordination template hypothesis"[47,48]. The enhanced stability of metal complexes of macrocyclic ligands over other linear polydentate ligands is attributed to various structural effects.

- Chelate effect- the linking of two donor atoms together with the metal ion results in a chelate. Such a linkage results in a large increase in the binding constants with metal ions as compared to the separate donor groups. This increased inertness is called as chelate effect, which is largely entropic in origin.
- Macrocyclic effect- the enhancement of the formation constants relative to the values for the thermodynamically most favored, structurally analogous, but non cyclic-amine has been termed as macrocyclic effect by analogy with the chelate effect.
- Cryptate effect- addition of a second ring to a macrocycle (resulting in a macrobiyclic ligand), further enhances the stability of its metal complexes. As for the change observed in transition from chelate to macrocyclic effects, the cryptate effect is often even higher than would be expected for simple addition of a second fused macrocycle.

The general observation displays that the affinity between the ligands of a particular kind, e.g., amines for a given metal increases with the increasing topological constraint[49] of the ligand system. The topological constraint is in the order, simple coordination < chelation < macrocyclic effect < cryptate effect **Figure 7**.

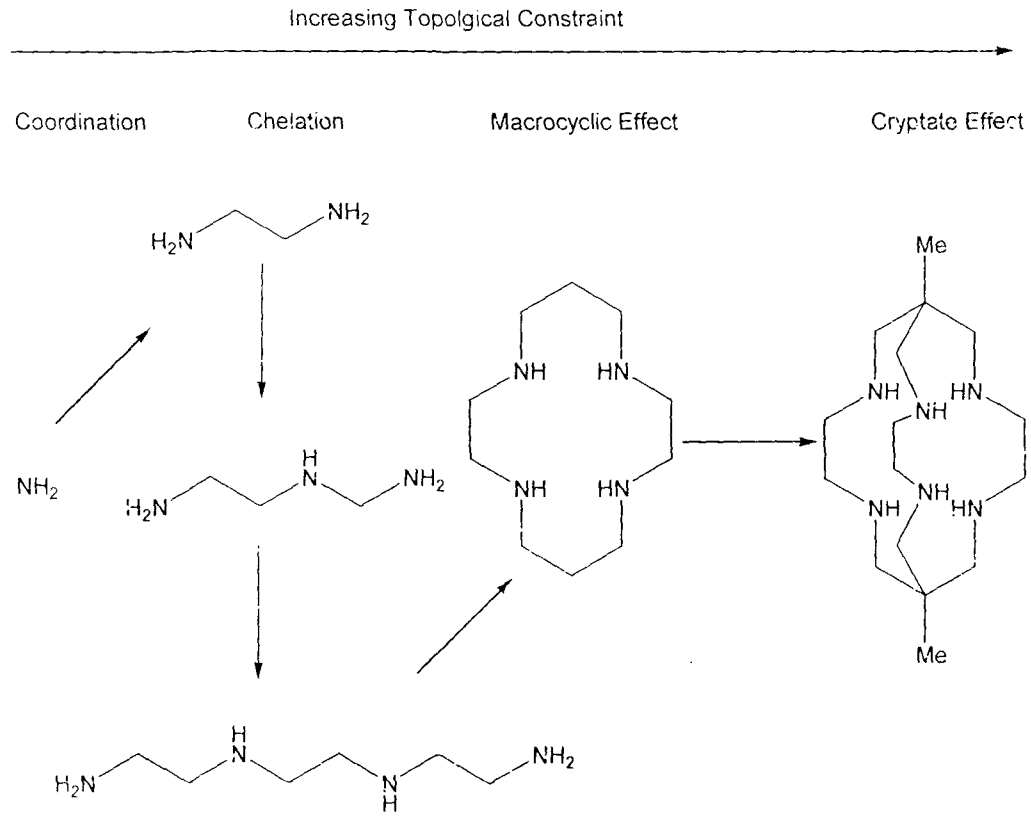
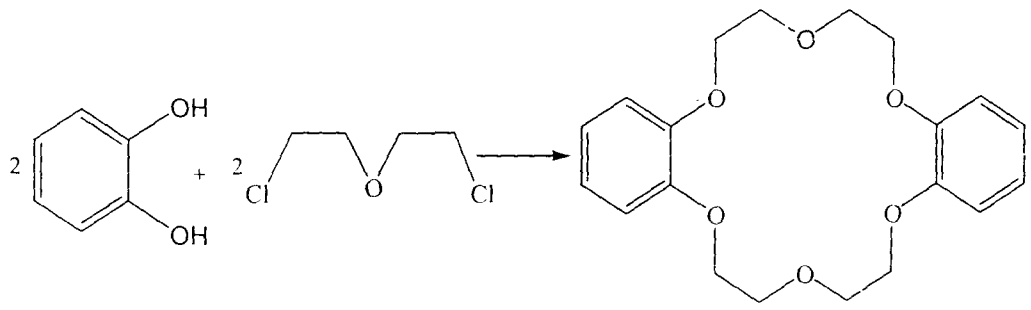
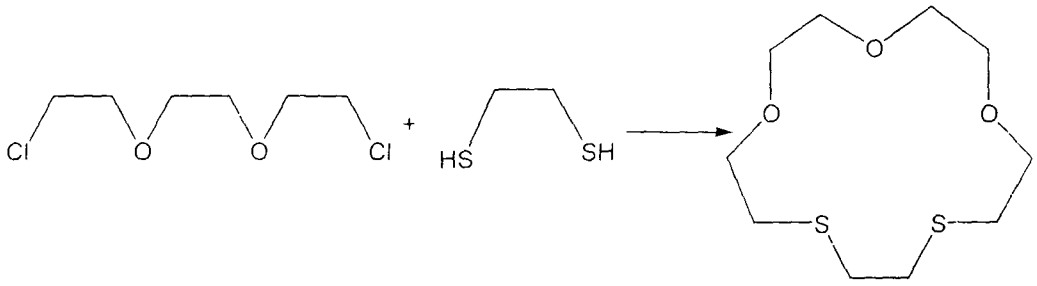



**Figure 7**

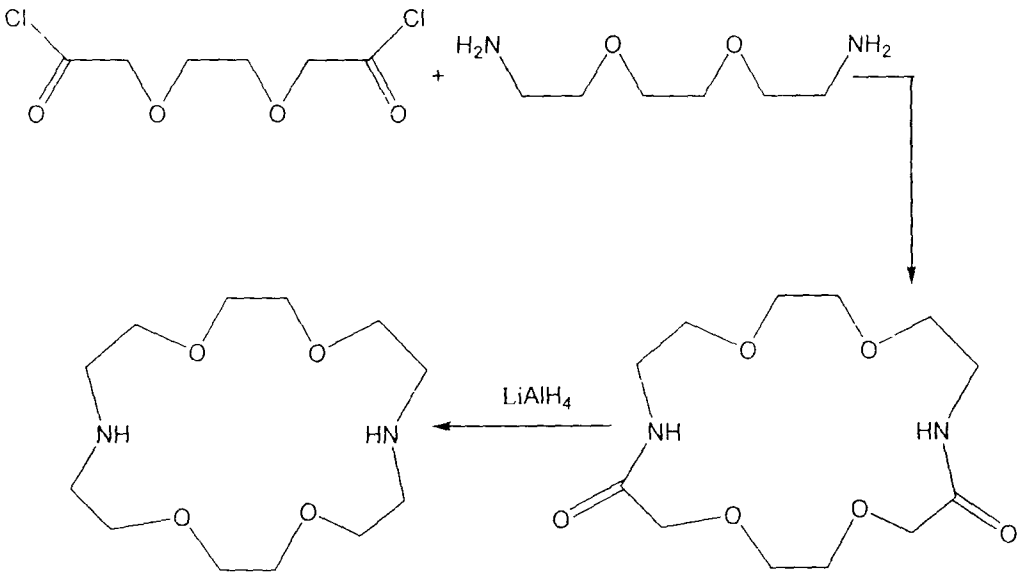
Macrocycles of the rigid types such as small cryptands and other preorganized macrocycles discriminate between cations that are either smaller or larger than the one with optimum size – "peak selectivity". Macrocycles of flexible type, such as larger crown ethers and large cryptands discriminate principally among smaller cations – "plateau selectivity"[50]. Cyclic polyethers have the largest affinities for the alkali, alkaline earth and lanthanide cations as the oxygen present in the polyether ring is a hard atom and prefers to complex with hard metal ion. The importance of crown ethers has been well recognized in separations, solubilizations, ion transport of inorganic salts, anion activation and enantiomeric selection of organic salts[51-55]. A variety of crown polyethers, mixed oxa-thia crowns and oxa-aza crowns have been prepared mainly by the direct synthesis[56-58] **Scheme 1-3**.




**Scheme 1**

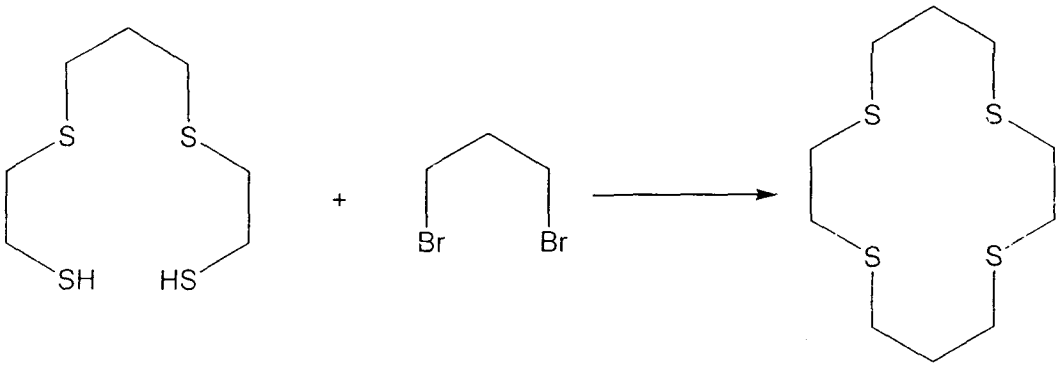



**Scheme 2**

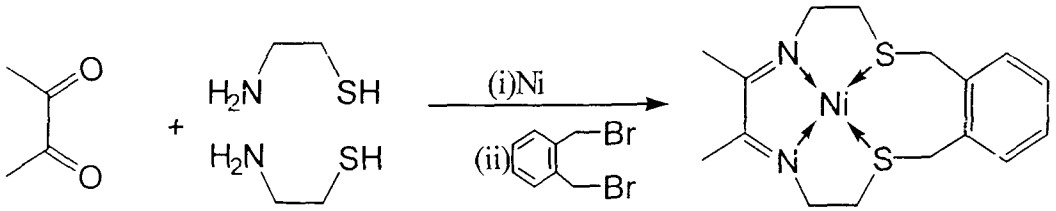



**Scheme 3**

Polythia macrocycles have been synthesized by reacting an appropriate polythiane with a dibromoalkane **Scheme 4 and 5**. The reaction may be sometimes aided by metal template[59,60].




**Scheme 4**




**Scheme 5**

Macrocyclic ligands incorporating sulfur donors show a preference to bind transition metal ion rather than alkali and alkaline earth ions due to the soft nature of the sulfur. An important aspect of the chemistry of these ligands pertains to the preference of the free ligand for the exodentate conformations in which the sulfur atoms are directed outwards[61] **Figure 8.**

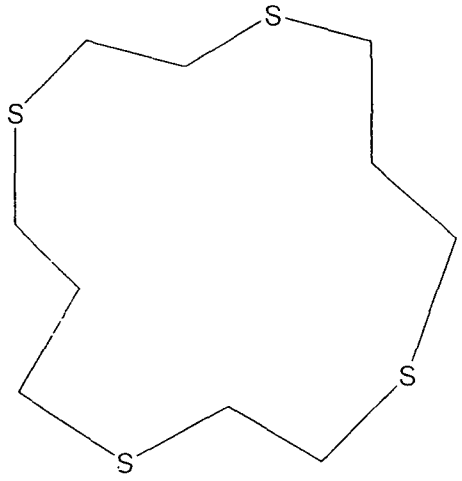



**Figure 8**

A number of macrocycles containing mixed donor atoms **Figure 9 and 10** have also been prepared[62-64] which coordinates to transition metal ion with favorable coordination geometry expected due to their ability to twist.

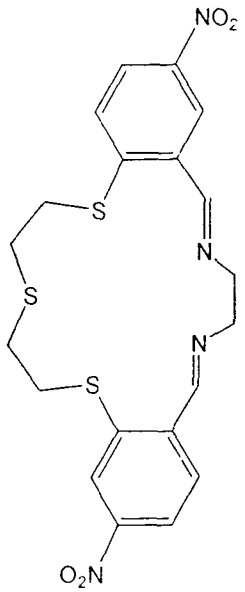



**Figure 9**

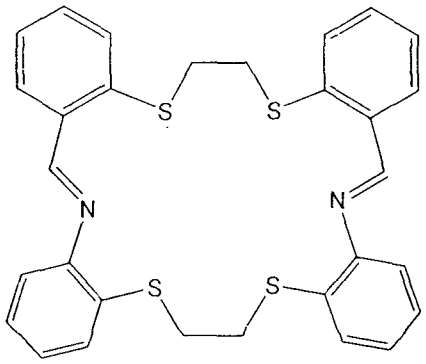
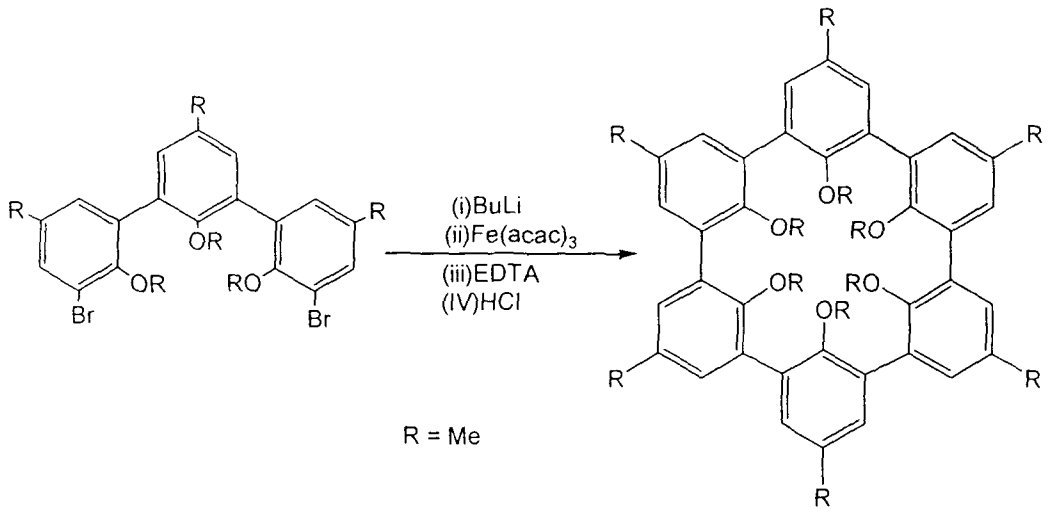



**Figure 10**

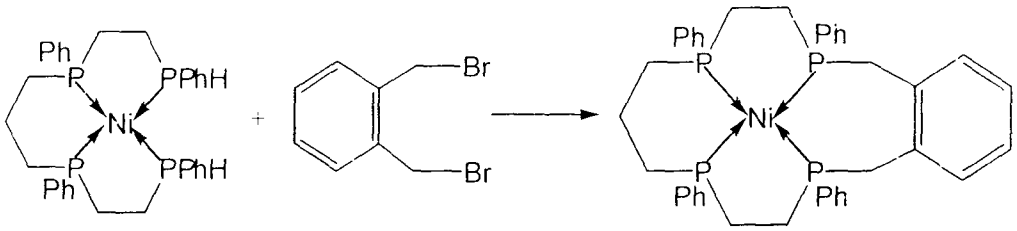
The synthesis of spherands involves ring closures using aryllithium with $Fe(acac)_3$. However, the yields increase by adopting high dilution techniques[41, 67] **Scheme 8.**




**Scheme 8**

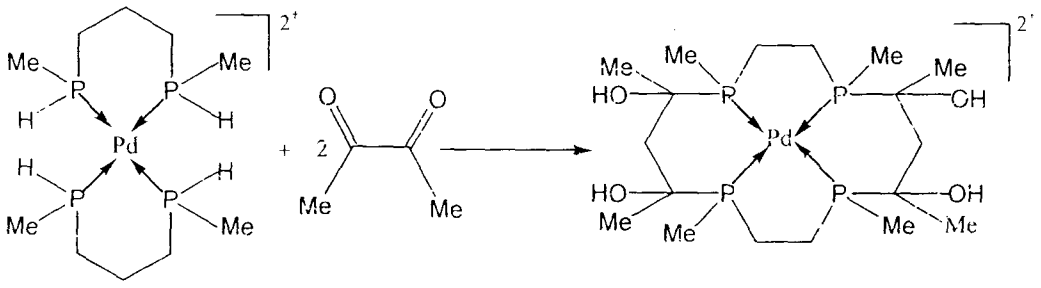
In case of calixarenes and spherands the match between the cation and the macrocyclic cavity is visible. In these cases, size selectivity goes together with the lack of flexibility of the ring, which is too rigid to undergo conformational changes upon complexation. The influence of cavity shape is envisaged in some calixerenes[68] which exhibit very high "coordination geometry selectivity" towards $UO_2^{2+}$.

The polyphospha macrocycles are capable of complexing a variety of metal ions, notably nickel, palladium and platinum. The phosphorus macrocycles[65], have been synthesized via template condensation of coordinated polyphosphine ligands and a dibromoalkane as shown in **Scheme 6.**



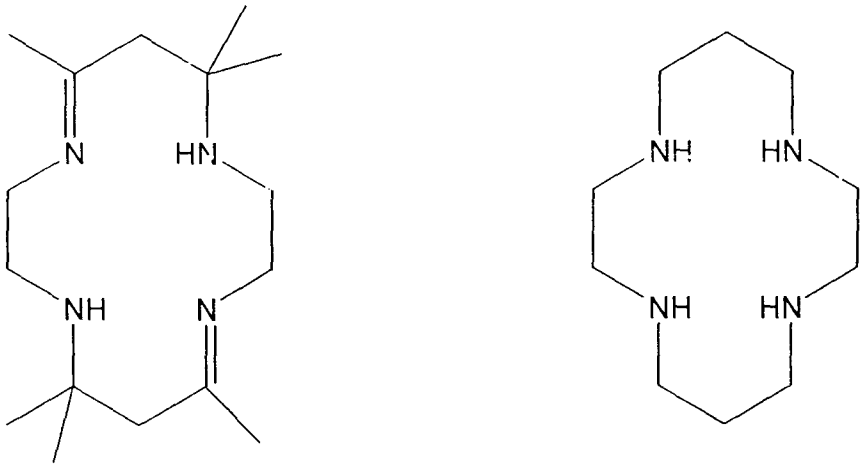

**Scheme 6**

Template assisted single-stage ring closure methods have also been reported[66] **Scheme 7.**




**Scheme 7**

The majority of all the nitrogen donor macrocycles (azamacrocycles) that have been studied are quadridentate as shown in **Figure 11a and 11b**. To fully encircle a first row transition metal ion, a macrocyclic ring size of between 12- and 16-membered is required, provided that the nitrogen donors are spaced in such a way leading to to five-, six-, or seven-membered chelate ring on coordination[69,70].



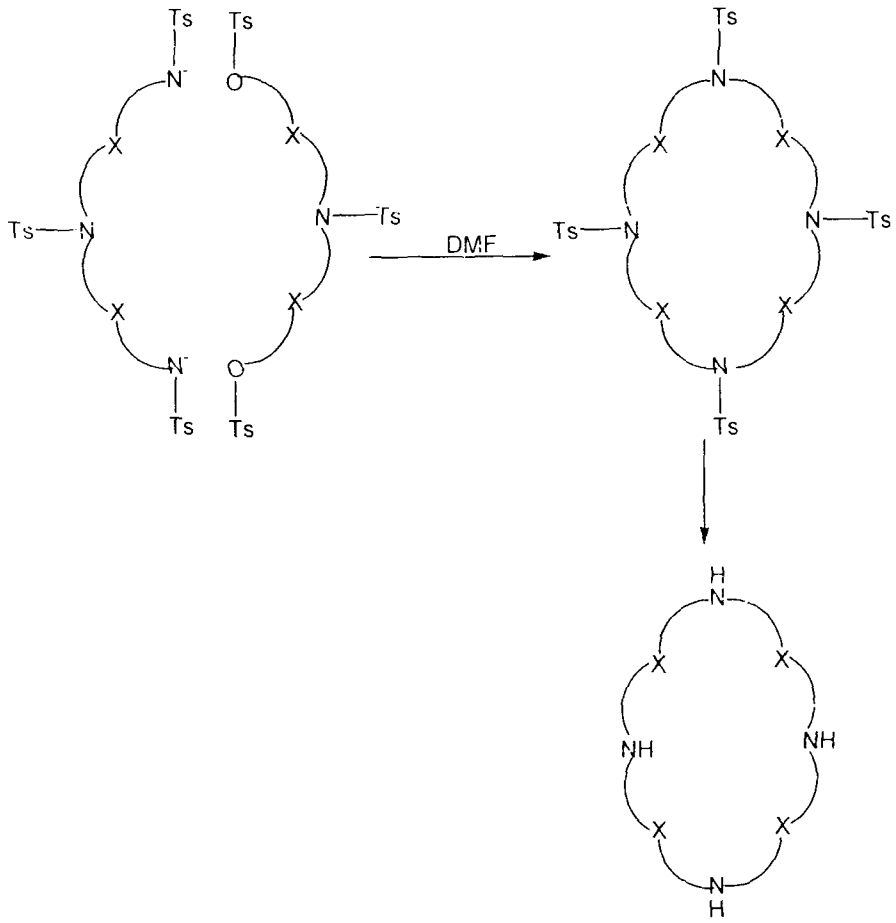

(a) (b)

**Figure 11**

The main target in a macrocyclic design is to synthesize macrocycles, which are able to discriminate among the different metal cations. The macrocyclic ligand also offers versatile molecular scaffolding for the coordinated ions. The

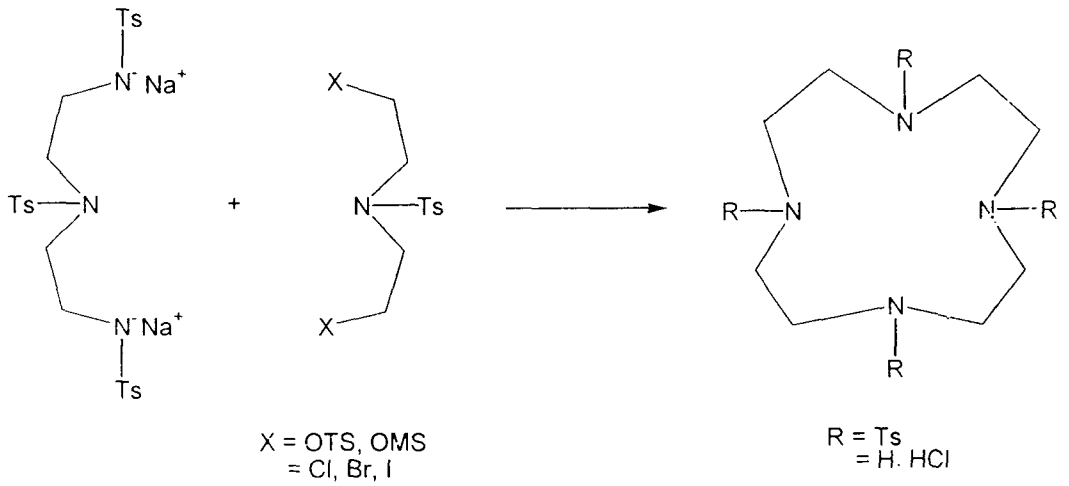
scaffolding provides its own structural rigidity or flexibility and may also protect the structure from the environment. The macrocyclic cavity fixes the metal ion and conveys the idea about the flexibility and the internuclear distance[71]. To achieve a desired azamacrocyclic ligand and their complexes various synthetic strategies have been developed, (a) Conventational Organic Synthesis (b) Metal-ion Promoted Synthesis (c) Modification of a Compound prepared by (a) and (b).

The unsubustituted-saturated azamacrocycles, the family of cyclic secondary amines, are generally prepared by the conventional synthesis. Similarly, other types of azamacrocycle, particularly cyclic amides[72] and macrocycles with N=CRCR=CRNH functions are also prepared conventionally. Typically in these preparations the cyclization reaction is performed under conditions of moderate to high dilution in order to minimize competing polymerization reactions. A typical example is the condensation of tosylated reactants by heating in presence of DMF at 100°C for 1h. The tetratosyl derivative was obtained in 80% yield. The tosyl groups were readily removed by heating this product in concentrated sulfuric acid as shown in **Scheme 9.**




**Scheme 9**

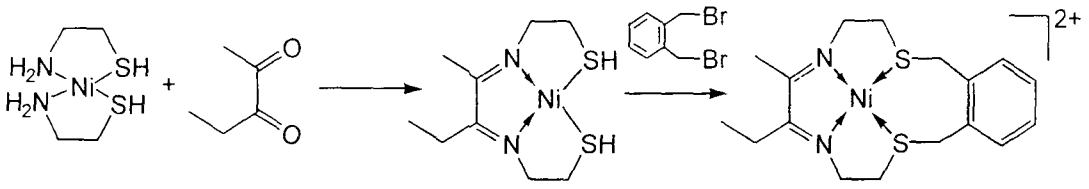
Stetter and Ross reported[73] moderate cyclization yields in the condensation of terminal dihalides with bissulfonamide sodium salts under high dilution but Richman and Atkins[74] found that by using performed bissulfonamide sodium salts and sulfonate ester leaving groups in a dipolar aprotic solvent obviates the high dilution technique as shown in **Scheme 10**.



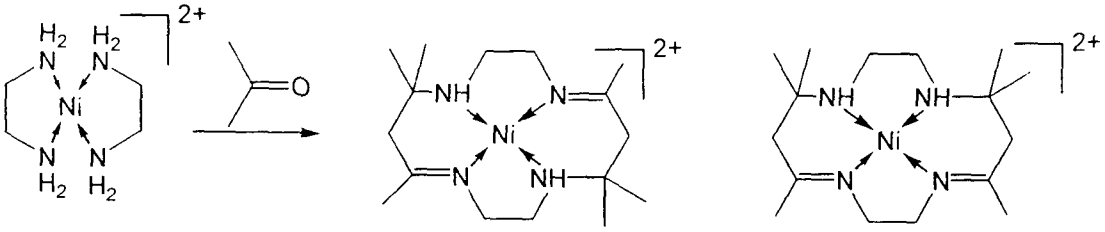

**Scheme 10**

A variety of azamacrocyclic complexes have been formed by the condensation reactions in the presence of a metal ion, known as metal ion promoted synthesis[75-77] or template synthesis. The majority of such reactions have imine formation as ring-closing step. The metal ion plays an important role in directing the steric course of the condensation reaction, as the metal ion template orients the reacting groups of linear substrates in a desired conformation and the favorable enthalpy of formation of metal-ligand bonds overcome the unfavorable entropy of the ordering of the multidentate ligand around the metal ion and hence promotes cyclization and this effect has been termed as "metal template effect"[78]. The template effect can be divided into two slightly more specific effects, the kinetic template effect describes the directive influence of the metal ion controls the steric course of a sequence of stepwise

reactions. In cases where the thermodynamic template effect operates, the metal ion perturbs an existing equilibrium in an organic system and the required product is produced often in high yield as a metal complex. In most cases, the kinetic template effect is operative, however an assignment cannot be made in all cases. The first example of the deliberate synthesis of tetraazamarocycle using the metal template method was described[79] by Thompson and Busch **Scheme 11**. Although Curtis has purely demonstrated the potential of template assembly by the reaction of $[Ni(en)_3]$ $(ClO_4)_2$ (en=1,2-diaminoethane) and acetone yielding isomeric tetraazamacrocyclic complexes[80] of Ni(II) **Scheme 12**.

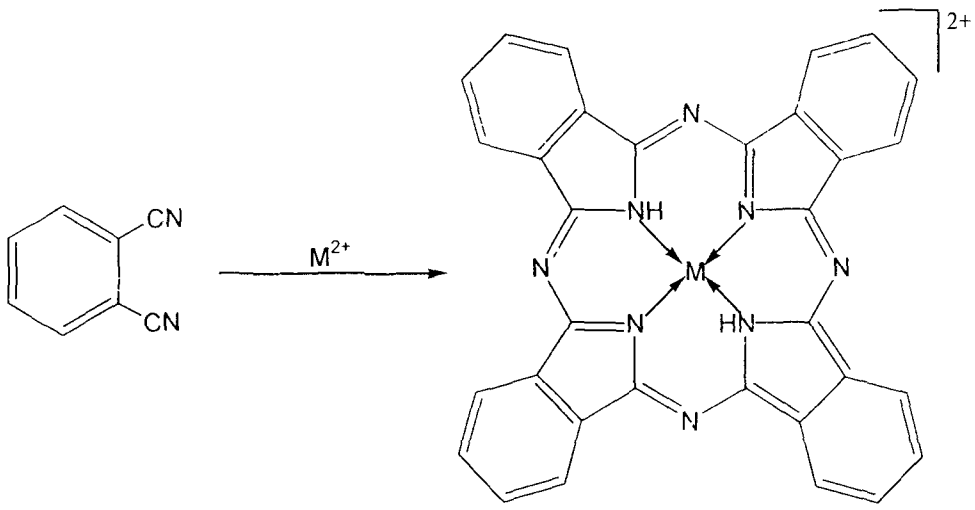


**Scheme 11**



**Scheme 12**

Metal ion also facilitates the self-condensation of o-phthalonitrile to give metal phthalocyanin complexes[81] **Scheme 13**. Shakir et.al. have reported[82] the self-condensation reaction of o-aminobenzoic acid in presence of transition metal ions as templates.




**Scheme 13**

Bosnich et.al. reported[83,84] studies on complexes of tetraazmacrocyclic ligands exhibiting exceptional properties due to the cyclic nature of these ligands. The saturated nitrogens are relatively hard and interact with metal ion through σ-bonds. The structural studies are related in terms of various effects such as chelate ring size, degree of unsaturation, spin state, redox behavior and other properties.

Schiff base macrocycles and their complexes are among the most studied macrocycles. These macrocycles have played a vital role in the development of synthetic macrocycles. Schiff base macrocycles are formed by the condensation between a dicarbonyl and a diamine resulting in imine linkages. The diimine Schiff base macrocycles obtained by the condensation of one molecule each of the dicarbonyl and diamine precursors have been termed as "1+1" macrocycles and the tetraimine macrocycles obtained by the condensation of two molecules of the dicarbonyl compound with the two molecules of diamine moiety have been termed as "2+2" macrocycles as a consequence of the number of the head and lateral units present[85-87]. The formation of "1+1" and "2+2" macrocycles by the metal template method is governed by the fact that if the reaction proceeds by an intramolecular mechanism it gives the "1+1" macrocycle or via the bimolecular mechanism it leads to the formation of "2+2" macrocycle **Figure 12**. The preference for the formation of "1+1" and "2+2" macrocycles in metal template condensation also depends upon the following factors:

- If the diamine have insufficient chain length to span the two carbonyl groups than "1+1" macrocycle cannot be formed[88].

- If the template ion is large with respect to cavity size of the "1+1" ring, a "2+2" condensation may occur[89,90].
- The electronic nature of metal ion such as charge, polarizability and the required geometry of the complex.
- Conformation of "1+1" acyclic chelate.

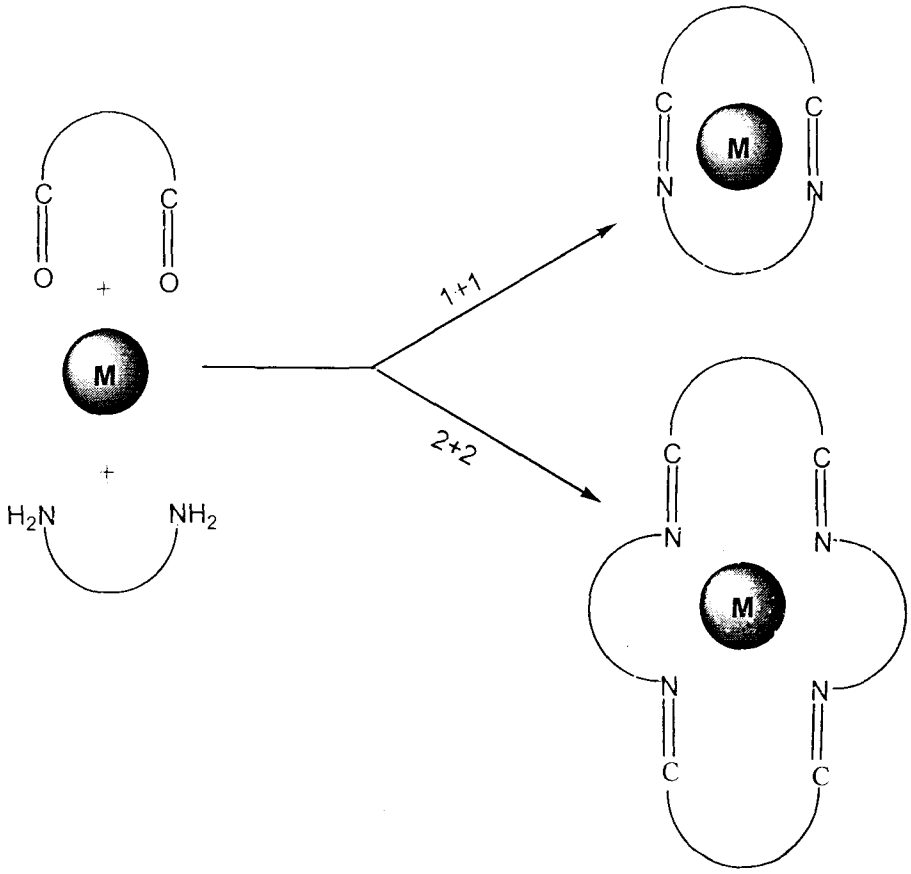
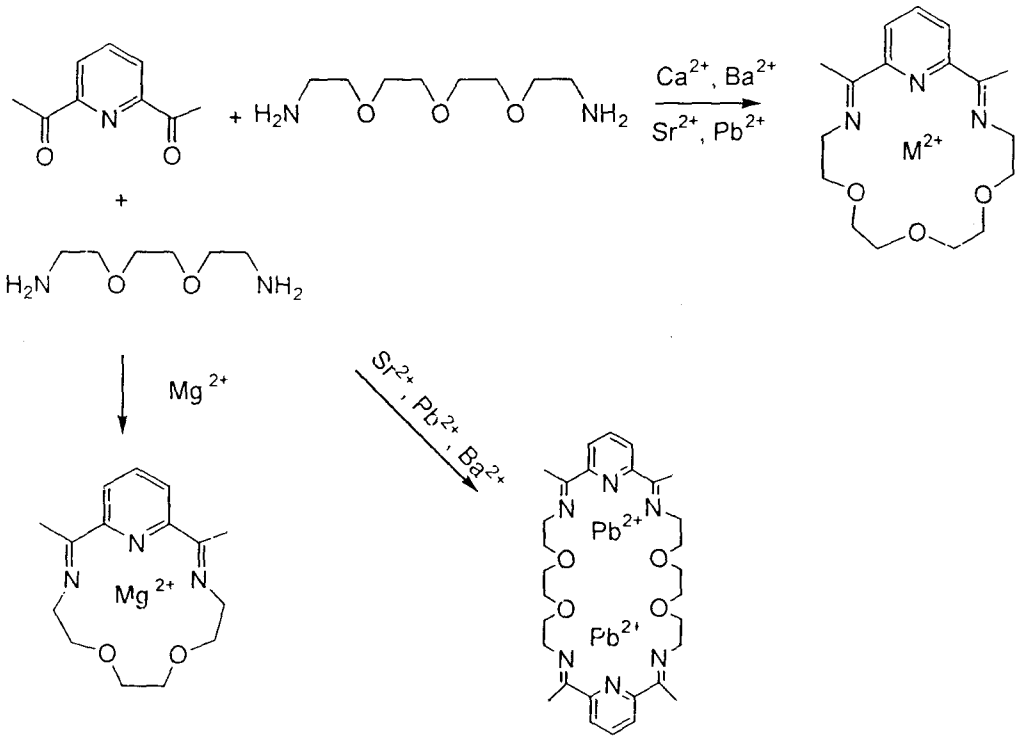



**Figure 12.** Metal templated synthesis of "1+1" and "2+2" macrocycle.

The template potential of a metal ion in the formation of a Schiff base macrocycle depends on the preference of the cations for stereochemistries (octahedral, tetragonal, square planar or square pyramidal) in which the bonding d-orbital are in orthogonal arrangements[91,92]. The size of the cation is important to direct the Schiff base condensation, as there should be compatibility between the radius of the templating cation and the hole or cavity of the macrocyclic framework. As indicated by Cation-Cavity "Best fit" The smaller metal ion favor the formation of "1+1" macrocycle while a larger metal ion favor the "2+2" macrocycle **Scheme 14.**




**Scheme 14**

For the synthesis of Schiff base macrocycles, dicarbonyl precursors and a wide variety of diamines have been used[93]. Among these precursors 2,6-diformyl-4-methyl-phenol was the first one applied for the preparation of macrocyclic Schiff base by Pilkington and Robson[94] in 1970 via template method. The earliest example of a synthetic macrocyclic ligand containing an imine linkage stems from the work of Curtis, which was derived from the mixed-aldol condensation of acetone with nickel(II) ethylenediamine complexes[77]. Curry and Busch reported[95] the iron(II) templated condensation reaction of 2,6-diacetylpyridine with triethylenetetraamine to give iron(III) complexes of a pentaazadiaminomacrocycle. In the recent past several 12-18 membered Schiff base macrocyclic ligands and their complexes have been reported[96-102] by several workers **Figure 13 and 14**.

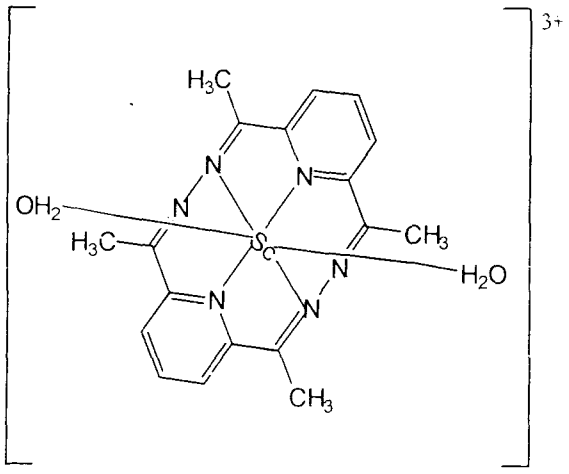



**Figure 13**

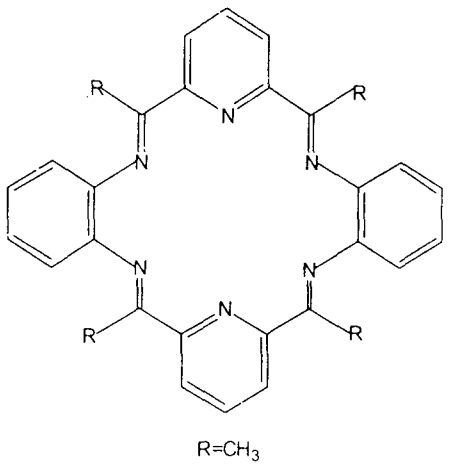
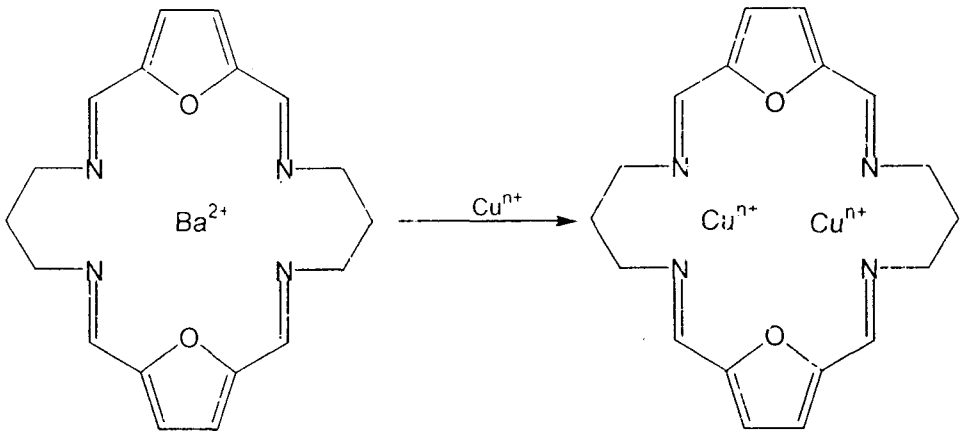


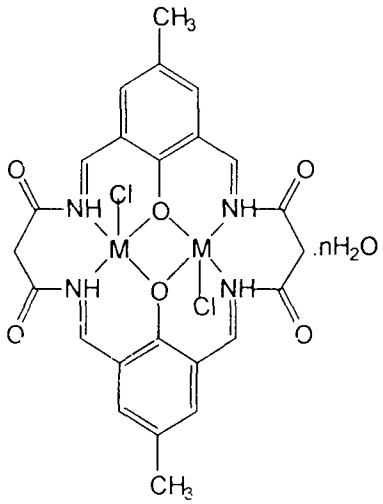

**Figure 14**

For large Schiff base macrocycles, the transition metal cations are ineffective as templates[103]. Therefore, the kinetic liability of the metal present in the generation of macrocyclic complexes derived from the use of alkaline earth metal and main group templating agent has enabled the generation of the corresponding transition metal complexes via transmetallation reaction[85,86,104] **Scheme 15**. This approach has been particularly successful when applied to generation of dinuclear Cu(II) complexes of tetraimine Schiff base macrocycles which have been used as speculative model for bimetallobiosites in cuproprotiens such as heamocyanin and tyrosinase[105].



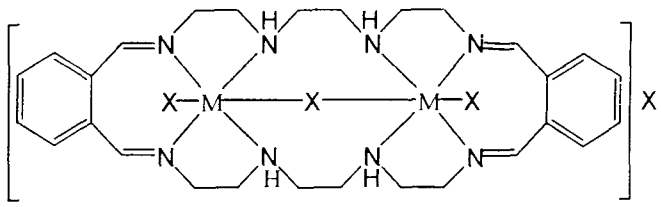

**Scheme 15**

The design and synthesis of binuclear ligands and their transition metal complexes have attracted increasing interest in recent years. The organization provided by an appropriately designed binucleating ligand can confer upon its derived complexes unusual structural features[106], and unusual reactivity including catalytic properties[107]. Such complexes, moreover, provides useful models for certain proteins containing pairs of metal centers and in investigation concerning the mutual influence of two metal centers on electronic, magnetic and electrochemical properties of such closely spaced paramagnetic centers[108-110]. The natural products such as hemerythrin[111] and heamocyanin[112] in which reversible dioxygen binding is associated with pairs of metal ions in close proximity helped to stimulate attention towards binuclear coordination compounds. A variety of binuclear macrocyclic ligands with two similar metal centers have been reported[113,114] **Figure 15 and 16.** Binuclear macrocyclic complexes having similar and dissimilar coordination sites are of particular interest because such macrocyclic complexes are thermodynamically stabilized and kinetically retarded with regard to metal dissociation and metal substitution relative to metal complexes of acyclic ligands[115,116]. Martell et.al. have reported[117-119] wide variety of polyazamacrocyclic Schiff base binucleating complexes with different bridging atoms or groups, in which an elegant note[119] about the catalytic activities of Cu(I) and Cu(II) has been added.




M=Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II).
n= 1-3.

**Figure 15**




M=Co(II), Ni(II), Cu(II) and Zn(II), X=Cl, Br

**Figure 16**

Macrocyclic ligand with pendant donor groups represents another class of ligands deliberately synthesized to achieve metal ion discrimination. Several examples of pendant arm macrocycles are known in which incorporation of functionalized pendant coordinating groups such as methylenecarboxylate[120], methylenepyridyl[121], hydroxyalkyl[122] and methylenephosphonate[123], on polyaza compounds can provide additional coordinating function and hence enhance the complexing stability. Recently, a group of researchers have reported the synthesis of hexaaza and octaazamacrocycles[124] bearing 2-hydroxy-3,5-dimethylbenzyl as pendant arms **Figure 17**.

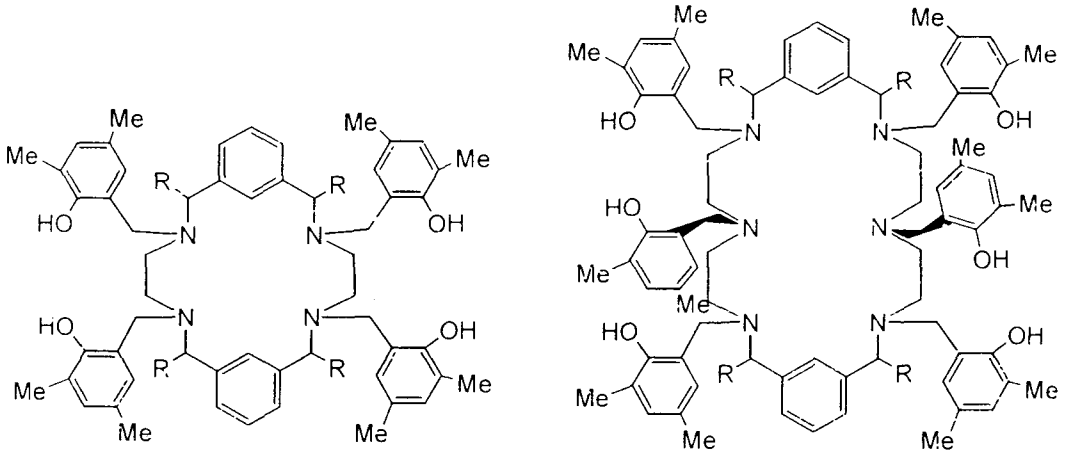
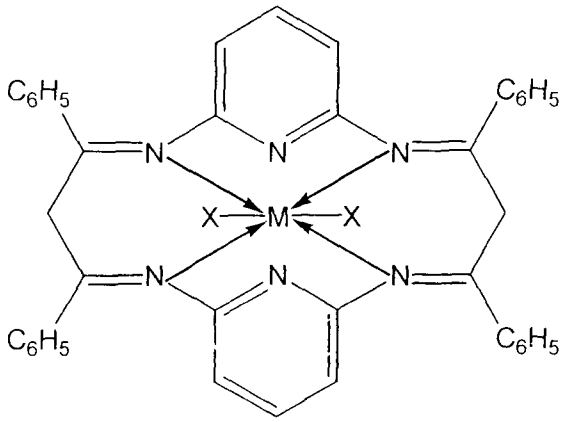


**Figure 17**

Functionalized pendant arm macrocycles have been successfully employed in the synthesis of metal chelating agents for medical applications owing to the kinetic inertness of the complexes, which make them resistant to decomplexation[125,126]. Kanda et.al. discussed the preparation of tetradentate Schiff base ligand having a pendant thioether function[127].

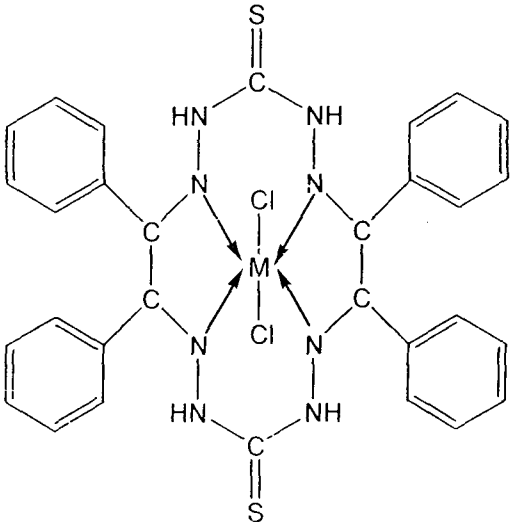
Macrocycles especially the ones possessing aromatic moieties are known to form charge transfer complexes with a variety of guests. These macrocycles were used to study complexation of diverse guests so as to provide new insights into non-covalent binding interaction, chiefly cation π-interactions[128,129]. These molecular interactions are formed between the electron rich π-orbital of an aromatic ring and a cation. Several macrocycles containing aromatic moieties have been reported[130-132] having 2,6-

diaminopyridine **Figure 18**, benzil **Figure 19** and o-phenylenediamine **Figure 20** subunits as the main part of the structural backbone of the macrocyclic framework.




M=Co(II), Ni(II) and Cu(II); X=Cl, Br, $NO_3$ and NCS.

**Figure 18**




M=Co(II), Ni(II), Cu(II) or Zn(II)
X=Cl, $NO_3$, or $CH_3COO$

**Figure 19**

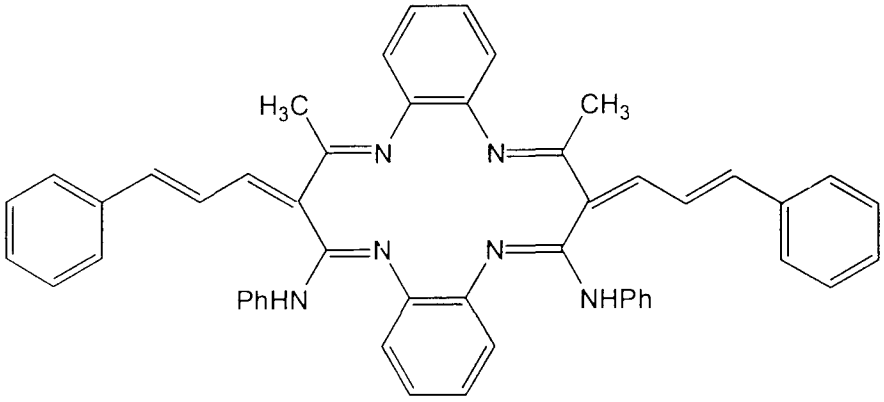
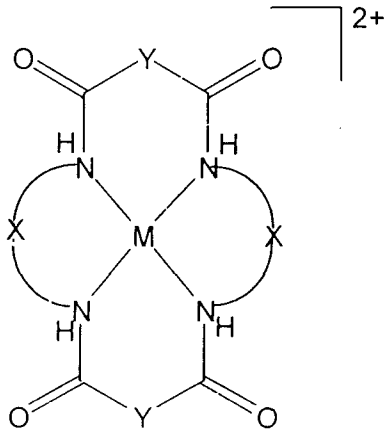


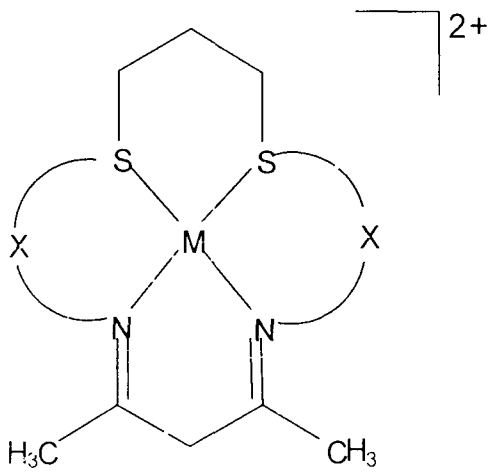

**Figure 20**

Shakir et.al. have reported a number of macrocycles and their transition metal complexes of varying ring sizes[133-136] **Figure 21**, macrocyclic complexes with mixed donors[137,138] **Figure 22**, binuclear macrocycles[139-141] **Figure 23**, aromatic macrocycles[142-145] **Figure 24**, etc.



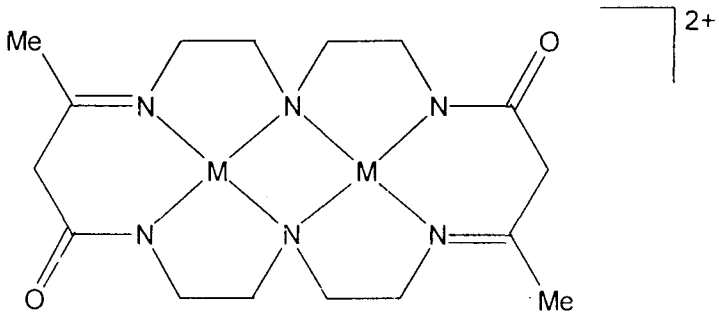

M = Ni(II), Cu(II), Zn(II), X = $(CH_2)_3$ and Y = $(CH_2)_4$

**Figure 21**



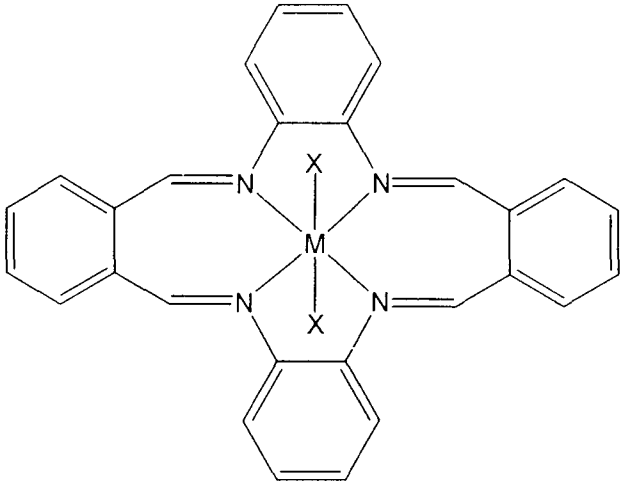

M = Co(II), Ni(II), Cu(II)
X = $(CH_2)_2$ or $C_6H_4$

**Figure 22**




M = Cu(II), Zn(II)

**Figure 23**




M=Co(II), Ni(II), Cu(II) and Zn(II)
X=Cl or $NO_3$

**Figure 24**

The brief introduction comprehends the research work carried out by some of the well-known scientists in the field of macrocyclic chemistry throughout the world and in this laboratory. Macrocyclic chemistry still forms the basis of more extensive exploration and research for their multi-dimensional utilities in the knowledge of the subject as well as in the wide range of applications. In view of the continued interest in the field of macrocyclic chemistry, it was thought worthwhile to synthesize and characterize novel tetraaza schiff base macrocyclic complexes with a few first row transition metal ions.

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# CHAPTER-2

# Experimental Methods

# 2.1 INSTRUMENTAL METHODS

There are several physico-chemical methods available for the study of coordination compounds and a brief description of the techniques used in the investigation of the newly synthesized complexes described in the present work are given below:

1- Infrared Spectroscopy

2- Nuclear Magnetic Resonance Spectroscopy

3- Electron Paramagnetic Resonance Spectroscopy

4- Ultraviolet and Visible (Ligand Field) Spectroscopy

5- Magnetic Susceptibility Measurements

6- Molar Conductance Measurements

7- Mass Spectrometry

8- Elemental Analyses

9- Job's Method

## 2.1.1 INFRARED SPECTROSCOPY

The term "infra red" covers the range of the electromagnetic spectrum between 0.78 and 1000 μm. In the context of infra red spectroscopy, wavelength is measured in "wavenumbers", which have the unit's $cm^{-1}$.

wavenumber = 1 / wavelength in centimeters

It is useful to divide the infrared range into three regions; *near*, *mid* and *far* infrared;

| **Region** | **Wavelength range** (μm) | **Wavenumber range** ($cm^{-1}$) |
|---|---|---|
| Near | 0.78 - 2.5 | 12800 – 4000 |
| Middle | 2.5 – 50 | 4000 – 200 |
| Far | 50 –1000 | 200 – 10 |

**Theory of infrared absorption**

IR radiation does not have enough energy to induce electronic transitions. Absorption of IR is restricted to compounds with small energy differences in the possible vibrational and rotational states.

For a molecule to absorb IR, the vibrations or rotations within a molecule must cause a net change in the dipole moment of the molecule. The alternating electrical field of the radiation (electromagnetic radation consists of an oscillating electrical field and an oscillating magnetic field, perpendicular to each other) interacts with fluctuations in the dipole moment of the molecule. If the frequency of the radiation matches the vibrational frequency of the molecule then radiation will be absorbed, causing a change in the amplitude of molecular vibration. In the absorption of the radiation, only transition for which

change in the vibrational energy level is $\Delta V=1$ can occur, since most of the transition will occur from stable $V_0$ to $V_1$ the frequency corresponding to its energy is called the fundamental frequency.

The group frequencies of certain groups are characteristic of the group irrespective of the nature of the molecule in which these groups are attached. The absence of any band in the approximate region indicates the absence of that particular group in the molecule.

**Molecular rotations**

Rotational levels are quantized, and absorption of IR by gases yields line spectra. However, in liquids or solids, these lines broaden into a continuum due to molecular collisions and other interactions.

**Molecular vibrations**

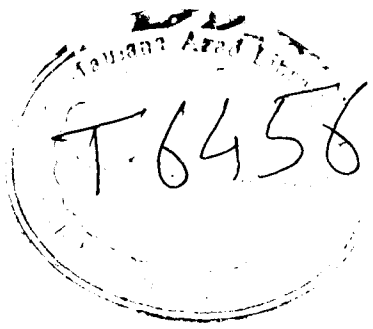
The positions of atoms in a molecule are not fixed; they are subject to a number of different vibrations. Vibrations fall into the two main catagories of *stretching* and *bending*.

**Stretching:** Change in inter-atomic distance along bond axis

- Symmetric
- Asymmetric

**Bending:** Change in angle between two bonds. There are four types of bend:

- Rocking : In-plane Rocking
- Scissoring : In-plane Scissoring
- Wagging : Out-of-plane Wagging
- Twisting : Out-of-plane Twisting




**Vibrational coupling**

In addition to the vibrations mentioned above, interaction between vibrations can occur (coupling) if the vibrating bonds are joined to a single central atom. Vibrational coupling is influenced by a number of factors viz., strong coupling of stretching vibrations occurs when there is a common atom between the two vibrating bonds, coupling of bending vibrations occurs when there is a common bond between vibrating groups, coupling between a stretching vibration and a bending vibration occurs if the stretching bond is one side of an angle varied by bending vibration, coupling is greatest when the coupled groups have approximately equal energies, no coupling is seen between groups separated by two or more bonds.

**Important Group Frequencies in the IR Spectra Pertinent to the Discussion of the Newly Synthesized Compounds.**

**a) N–H Stretching Frequency**

The N–H Stretching vibrations occur in the region 3300-3500 $cm^{-1}$ in the dilute solution[1]. The N–H stretching band shifts to lower value in the solid state due to the extensive hydrogen bonding. Primary amines in the dilute solutions, in non-polar solvents give two absorptions i.e. symmetric stretch found near 3400 $cm^{-1}$ and asymmetric stretch mode found near 3500 $cm^{-1}$. Secondary amines show only a single N–H stretching band in dilute solutions. The intensity and frequency of N–H stretching vibrations of secondary amines are very sensitive to structural changes. The band is found in the range 3310-3350 $cm^{-1}$ (low intensity) in aliphatic, secondary amines and near 3490 $cm^{-1}$ which shows much higher intensity in heterocyclic secondary amines such as pyrazole and imidozole.

**b) C–N Stretching Frequency**

The C–N stretching absorption gives rise to strong bands in the region 1250-1350 $cm^{-1}$ in all the amines[1,2]. In primary aromatic amines there is one band in the region 1250-1340 $cm^{-1}$ but in secondary amines two

bands have been found in the regions 1280-1350 $cm^{-1}$ and 1230-1280 $cm^{-1}$.

**c) C=N Stretching Frequency**

Schiff bases (RCH=NR, imines), oximes, thiazoles, iminocarbonates etc. show the C=N stretching frequency in the 1471-1689 $cm^{-1}$ region[1,2]. Although the intensity of the C=N stretch is variable, however it is usually more intense than the C=C stretch.

**d) N–N Stretching Frequency**

A strong band appearing in the region around 1000 $cm^{-1}$ may reasonably be assigned[3] to ν (N–N) vibrations.

**e) M–N Stretching Frequency.**

The M–N stretching frequency is of particular interest since it provides direct information regarding the metal-nitrogen coordinate bond. Different amine complexes exhibited[2] the metal-nitrogen frequencies in the 300-450 $cm^{-1}$ region.

**f) M–X Stretching Frequency**

Metal-halogen stretching bands appear[2] in the region of 500-750 $cm^{-1}$ for M–F, 200-400 $cm^{-1}$ for M–Cl, 200-300 $cm^{-1}$ for M–Br and 100-200 $cm^{-1}$ for M–I.

**g) M–O Stretching Frequency**

Metal-oxygen stretching frequency has been reported to appear in different region for different metal complexes. The M–O stretching frequency of nitrato complexes lie in the range of 250-350 $cm^{-1}$. Furthermore, unidentate nitrate group display bands in the 1230-1260, 1020-1080 and 870-890 $cm^{-1}$ regions assigned[2] to ν (N–O) vibrations.

## 2.1.2 NUCLEAR MAGNETIC RESONANCE SPECTROSCOPY

### $^1$H- NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy is a powerful and theoretically complex analytical tool where experiments are performed on the nuclei of atoms. NMR spectroscopy is based on the measurement of electromagnetic radiations in the radio-frequency region of roughly 4 to 900 MHz. In contrast to ultraviolet, visible and infrared absorption, nuclei of atoms rather than outer electrons are involved in the absorption process. Nuclear magnetic resonance spectroscopy is one of the most powerful tools available to

the chemist and biochemist for elucidating the structure of chemical species. There are two types of spectrometers:

a. Continuous-Wave (CW).

b. Pulsed, or Fourier transform (FT-NMR)

All early studies were carried out with Continuous-Wave instruments. Fourier transform spectrometers were available commercially around 1970. In both types of instruments, the sample is positioned in a powerful magnetic field of strength of several teslas. The only nuclei that exhibit the NMR phenomenon are those for which spin quantum number "I" is greater than 0, the spin quantum number "I" is associated with the mass number and atomic number of the nuclei as follows:

| Mass number | Atomic number | Spin quantum number |
|---|---|---|
| Odd | Odd or Even | 1/2, 3/2, 5/2,..... |
| Even | Even | 0 |
| Even | Odd | 1, 2, 3,..... |

The nucleus of $^{1}H$ proton, has I = 1/2, whereas $^{12}C$ and $^{16}O$ have I = 0 and are therefore nonmagnetic. Nuclei for which, I = 1/2, include $^{1}H$, $^{13}C$, $^{19}F$ and $^{31}P$, while $^{2}H$ and $^{14}N$ have I = 1.

Nuclei of isotopes which possess an odd number of protons and odd number of neutrons or both exhibits mechanical spin phenomenon which are associated with angular momentum. This angular momentum is characterized by a nuclear spin quantum number, I such that, I = 1/2n, where n is an integral 0, 1, 2, 3. ----- -etc.

The nuclei with I = 0, do not possess spin angular momentum and do not exhibit magnetic resonance phenomena. The nuclei of $^{12}C$ and $^{16}O$ fall into this category. Nuclei for which I =1/2 include $^{1}H$, $^{19}F$, $^{13}C$, $^{31}P$ and $^{15}N$, while $^{2}H$ and $^{14}N$ have I = 1.

Since atomic nuclei are associated with charge, a spinning charged nucleus generates a magnetic field that is analogous to the field produced when electricity flows through a coil of wire. The resultant magnetic moment, $\mu$, is oriented along the axis of spin and is proportional to the angular momentum p. Thus,

$$\mu = \gamma p$$

Where, $\gamma$ is gyromagnetic ratio.

Under the influence of the external magnetic field, a magnetic nucleus can take up different orientation with respect to that field, the number of possible orientation is given by (2I+1), so that for nuclei with spin quantum number 1/2, ($^{1}H$, $^{13}C$, $^{19}F$, etc.) only two orientations are allowed.

If a proton is precessing in the aligned orientation, it can absorb energy and pass into the opposed orientation, subsequently it can loose this extra energy and relax back into the aligned position. If the precessed nuclei are irradiated with a beam of radiofrequency energy of the proper frequency, the lower energy nuclei will absorb this energy and move to a higher energy state. If the precessing frequency is the same as the frequency of the radio-frequency beam, the nucleus and the radio-frequency beam are said to be in resonance, hence the term Nuclear Magnetic Resonance.

NMR spectra can be recorded by either holding the magnetic field constant or scanning the radio-frequency or by keeping the radio-frequency constant and varying the magnetic field. The higher the operating frequency, the better will be the resolution, and thus easier the interpretation.

**$^{13}$C-NMR spectroscopy**

Carbon-13 has a nuclear spin (I = ½) and makes up 1.1% of naturally occurring carbon to make carbon nuclear magnetic resonance spectroscopy ($^{13}$C NMR) a useful technique. Since carbon is the element central to organic chemistry, $^{13}$C NMR plays an important role in determining the structure of unknown organic molecules and the study of organic reactions. In particular, the $^{13}$C NMR spectrum of an organic compound provides information concerning:

- the number of different types of carbon atoms present in the molecule

- the electronic environment of the different types of carbons
- the number of "neighbors" a carbon has (splitting)

The major differences between $^{13}C$ NMR and $^{1}H$ NMR spectra are:

- No integration of carbon spectra
- Wide range (0-200 ppm) of resonances for common carbon atoms (typical range for protons 1-10 ppm)

$^{13}C$ chemical shifts span slightly over 200 ppm in contrast to the typical 8 to 9 ppm range in the $^{1}H$ NMR, thus considerably more structural information is generally available from $^{13}C$ chemical shift data. Another very important difference between $^{1}H$ and $^{13}C$ NMR spectroscopy is that diamagnetic effects are dominant in the shielding of hydrogen nucleus, whereas paramagnetic effects are dominant contributors to the shielding of the $^{13}C$ nucleus. Long range shielding effects that are important in the $^{1}H$ NMR are less important in $^{13}C$ NMR. As a result, $^{13}C$ chemical shifts generally do not parallel $^{1}H$ chemical shifts. Since the spin number for $^{13}C$ is the same as for $^{1}H$, i.e; 1/2, the same rules apply for predicting the multiplicity of the absorption.

A $^{13}C$ NMR spectrum consists of discrete, sharp lines corresponding to each non-equivalent carbon atom. These resonances are typically in the range 0 to 220 ppm with the TMS reference peak at 0 ppm. The main feature of $^{13}C$ NMR

is its ability to give information concerning the chemical environment of carbon atoms. This helps to identify any functional groups present as well as giving clues towards the solution of the structure. The coupling constants for $^{13}C$-$^{1}H$ are large (100-250 Hz) and thus interpretation of the $^{13}C$ spectra can be difficult because of the overlapping $^{13}C$-$^{1}H$ multiplets. To simplify the spectrum, $^{13}C$ NMR spectra are generally recorded under double resonance conditions in which the coupling of $^{1}H$ to $^{13}C$ is destroyed. Complete $^{1}H$ coupling is accomplished by irradiating the $^{1}H$ resonance region with a broad band width radio-frequency radiation termed as "noise", sufficient to cover the entire $^{1}H$ resonance region. The $^{13}C$ NMR spectra thus obtained contain only singlet resonances corresponding to its chemical shifts.

### 2.1.3 ELECTRON SPIN RESONANCE SPECTROSCOPY

Electron paramagnetic resonance spectroscopy is a branch of absorption spectroscopy in which radiation of microwave frequency is absorbed by molecules possessing electron with unpaired spins. Gorter demonstrated[4,5] that a paramagnetic salt when placed in a high frequency alternating magnetic field absorbs energy which is influenced by the application of a static magnetic field either parallel or perpendicular to the alternating magnetic field. The degeneracy of a paramagnetic ion is lifted in a strong static magnetic field and the energy levels undergo a Zeeman splitting. Application of an oscillating

magnetic field of appropriate frequency will induce transitions between the Zeeman levels and the energy is absorbed from the electromagnetic field. If the static magnetic field is slowly varied, the absorption shows a series of maxima. The plot between the absorbed energy and the magnetic field is called the electron paramagnetic resonance spectrum.

A system of charges exhibit paramagnetism whenever it has a resultant angular momentum. Such paramagnetic system includes elements containing 3d, 4d, 5d, 5f, 6d etc., electrons, atoms having an odd number of electrons like hydrogen, molecules containing odd number of electrons such as $NO_2$, NO etc., and free radicals which posses an unpaired electron like methyl, diphenylpicryl hydrazide, are among the suitable reagents for EPR investigation. Splitting of energy levels in EPR occurs under the effect of two types of fields, namely the internal crystalline field and applied magnetic field. While studying a paramagnetic ion in a diamagnetic crystal lattice, two types of interactions are observed, i.e. interactions between the paramagnetic ions called dipolar interaction and the interactions between the paramagnetic ion and the diamagnetic neighbour called crystal field interaction. For small doping amount of paramagnetic ion in the diamagnetic host, the dipolar interaction will be negligibly small. The later interaction of paramagnetic ion with diamagnetic ligands modifies the magnetic properties of the paramagnetic ions. According

to crystal field theory, the ligand influences the magnetic ion through the electric field, which they produce at its site and their orbital motion gets modified. The crystal field interaction is affected by the outer electronic shells.

The dipole-dipole interaction arises from the influence of magnetic field of one paramagnetic ion on the dipole moments of the neighboring, similar ions. The local field at any given site will depend on the arrangements of the neighbors and the direction of their dipole moments. Thus the resultant magnetic field on the paramagnetic ion will be the vector sum of the external field and the local field. Thus resultant field varies from site to site giving a random displacement of the resonance frequency of each ions and thus broadening the line widths.

Hyperfine interactions are mainly magnetic dipole interactions between the electronic magnetic moment and the nuclear magnetic moment of the paramagnetic ion. The quartet structure in the EPR of vanadyl ion is the results of hyperfine interactions. The origin of this can be understood simply by assuming that the nuclear moment produces a magnetic field, $B_N$ at the magnetic electrons and the modified resonance condition will be $E = h\upsilon = g\beta |B + B_N|$ where $B_N$ takes up $2I+1$, where I is the nuclear spin. There may be an additional hyperfine structure also due to interaction between magnetic electrons and the surrounding nuclei called super hyperfine structure. The effect

was first observed by Owens and Stevens in ammonium hexa chloroiridate[6] and subsequently for a number of transition metal ions in various hosts[7,8].

### 2.1.4 ULTRA-VIOLET AND VISIBLE (LIGAND FIELD) SPECTROSCOPY

Most of the compounds absorb light somewhere in the spectral region between 200 and 1000 nm. These transitions correspond to the excitation of electrons of the molecules from ground state to higher electronic states. In a transition metal all the five d-orbitals viz. $d_{xy}$, $d_{yz}$, $d_{xz}$, $d_z^2$ and $d_{x^2-y^2}$ are degenerate. However, in coordination compounds due to the presence of ligands this degeneracy is lifted and d-orbitals split into two groups called $t_{2g}$ ($d_{xy}$, $d_{yz}$ and $d_{xz}$) and $e_g$ ($d_z^2$ and $d_{x^2-y^2}$) in an octahedral complex and t and e in a tetrahedral complex. The set of $t_{2g}$ orbitals goes below and the set of $e_g$ orbitals goes above the original level of the degenerate orbitals in an octahedral complex. In case of the tetrahedral complexes the position of the two sets of the orbitals is reversed, the e going below and t going above the original degenerate level. When a molecule absorbs radiation, its energy can be expressed by the relation:

$$E = h\nu$$

$$or\ E = hc/\lambda$$

Where h is Planck's constant, ν and λ are the frequency and wavelength of the radiation, respectively and c is the velocity of the light.

In order to interpret the spectra of transition metal complexes, the device of energy level diagram based upon "Russell Saunder Scheme" must be introduced. This has the effect of splitting the highly degenerate configurations into groups of levels having lower degeneracies known as "Term Symbols".

The orbital angular momentum of electrons in a filled shell vectorically adds up to zero. The total orbital angular momentum of an incomplete d shell electron is observed by adding L value of the individual electrons, which are treated as a vector with a component ml in the direction of the applied field. Thus

$L = \Sigma_i ml_i = 0, 1, 2, 3, 4, 5, 6,$

S, P, D, F, G, H, I

The total spin angular momentum $S = \Sigma_i s_i$ where $s_i$ is the value of spin angular momentum of the angular momentum of the individual electrons. The total spin angular momentum S has a degeneracy $\tau$ equal to $2S + 1$, which is also known as "Spin Multiplicity". Thus, a term is finally denoted as "$\tau L$". For example, if $S = 1$ and $L = 1$, the term will be $^3P$ and similarly if $S = 1\ ½$, and $L = 3$, the term will be $^4F$.

In general the terms arising from a $d^n$ configuration are as follows:

$d^1 d^9$ : $^2D$

$d^2\ d^8$ : $^3F, ^3P, ^1G, ^1D, ^1S$

$d^3\ d^7$ : $^4F, ^4P, ^2H, ^2G, ^2F, ^2D(2), ^2P$

$d^4\ d^6$ : $^5D, ^3H, ^3G, ^3F(2), ^3D, ^2P(2), ^1I, ^1G(2), ^1F, ^1D(2), ^1S(2)$

$d^5$ : $^4S, ^4G, ^4F, ^4D, ^4P, ^2I, ^2H, ^2G(2), ^2F(2), ^2D(3), ^2P, ^2S.$

Coupling of L and S also occurs, because both L and S if non-zero, generate magnetic fields and thus tend to orient their moments with respect to each other in the direction where their interaction energy is least. This coupling is known as "LS coupling" and gives rise to resultant angular momentum denoted by quantum number J which may have quantized positive values from | L + S | up to | L – S | e.g., in the case of $^3P$ (L = 1, S = 1), $^4F$ (L = 3, S = 1 ½) possible values of J representing state, arising from term splitting are 2,1 and 0 and 4 ½ , 3 ½, 2 ½, and 1 ½. Each state is specified by J is 2J + 1 fold degenerate. The total number of states obtained from a term is called the multiplet and each value of J associated with a given value of L is called component. Spectral transitions due to spin-orbit coupling in an atom or ion occurs between the components of two different multiplets while LS coupling scheme is used for the elements having atomic number less than 30. in that case spin-orbital interactions are large and electrons repulsion parameters decreases. The spin-angular momentum of an individual electron couples with its orbital momentum to give an individual J for that electron. The individual J's couple to

produce a resultant J for the atom. The electronic transitions taking place in an atom or ion are governed by certain "Selection Rules", which are as follows:

1. Transitions between states of different multiplicity are forbidden.
2. Transitions involving the excitation of more than one electron are forbidden.
3. In a molecule, which has a centre of symmetry, transitions between two gerade or two ungerade states are forbidden.

It is possible to examine the effects of crystal field on a polyelectron configuration. The ligand field splitting due to cubic field can be obtained by considerations of group theory. It has been shown that an S state remains unchanged. P states does not split, and D state splits into two and F state into three and G state into four states as tabulated below: (Applicable for an octahedral 'Oh' as well as tetrahedral 'Td' symmetry)

S ---------- $A_1$

P ---------- $T_1$

D ---------- $E + T_2$

F ---------- $A_2 + T_1 + T_2$

G ---------- $A_2 + E + T_1 + T_2$

Transitions from the ground state to the excited state occur according to the selection rules described earlier. The energy level order of the states arising from the splitting of a term state for a particular ion in an octahedral field is the reverse that of the ion in a tetrahedral field. However, due to transfer of charge from ligand to metal or metal to ligand, sometimes bands appear in the ultraviolet region of the spectrum. These spectra are known as "Charge Transfer Spectra" or "Redox Spectra". In metal complexes there are often possibilities that charge transfer spectra extend into the visible region to obscure d-d transition. However, these should be clearly discerned from the ligand bands, which might also occur in the same region.

### 2.1.5 MAGNETIC SUSCEPTIBILITY MEASUREMENTS

The determination of magnetic moments of transition metal complexes have been found to provide ample information in assigning their structure. The main contribution to bulk magnetic properties arises from magnetic moment resulting from the motion of electrons. It is possible to calculate the magnetic moment of known compounds from the measured values of magnetic susceptibility. There are several kinds of magnetism in substances viz. diamagnetism, paramagnetism and ferromagnetism or antiferromagnetism. Mostly compounds of the transition elements are paramagnetic. Diamagnetism is attributable to the closed shell electrons with an applied magnetic field. In the closed shell the

electron spin moment and orbital moment of the individual electrons balance one another so that there is no magnetic moment. Ferromagnetism and antiferromagnetism arise as a result of interaction between dipoles of neighbouring atoms.

If a substance is placed in a magnetic field H, the magnetic induction B with the substance is given by:

$$B = H + 4\pi I$$

Where I is the intensity of magnetization. The ratio B/H is called magnetic permeability of the material and is given by:

$$B/H = I + 4\pi(I/H) = I + 4\pi K$$

Where K is called the magnetic susceptibility per unit volume or volume susceptibility. B/H is the ratio of the density of lines of force within the substance to the density of such lines in the same region in the absence of sample. Thus, the volume susceptibility of a vacuum is by definition zero since in vacuum B/H = 1.

When magnetic susceptibility is considered on the weight basis, the gram susceptibility ($\chi_g$) is used instead of volume susceptibility. The $\mu_{eff}$ value can then be calculated from the gram susceptibility multiplied by the molecular weight and corrected for diamagnetic value as:

$$\mu_{eff} = 2 \cdot 84\sqrt{\chi_M^{corr} \cdot T}\ BM$$

Where, T is the absolute temperature at which the experiment is performed.

The magnetic properties of any individual atom or ion will result from some combination of these two properties that is the inherent spin moment of the electron and the orbital moment resulting from the motion of the electron around the nucleus. The magnetic moments are usually expressed in Bohr Magnetons (BM). The magnetic moment of a single electron is given by:

$$\mu_S = g\sqrt{S(S+1)}\ BM$$

Where S is the spin quantum number and g is the gyromagnetic ratio. For $Mn^{2+}$, $Fe^{3+}$ and other ions whose ground states are S states there is no orbital angular momentum. In general however, the transition metal ion in their ground state D or F being most common, do possess orbital angular momentum. For such ions, as $Co^{2+}$ and $Ni^{2+}$, the magnetic moment is given by

$$\mu_{(S+L)} = g\sqrt{4S(S+1) + L(L+1)}$$

In which L represents the orbital angular momentum quantum number for the ion.

The spin magnetic moment is insensitive to the environment of metal ion, the orbital magnetic moment is not. In order for an electron to have an orbital angular momentum and thereby an orbital magnetic moment with reference to a

given axis, it must be possible to transform the orbital into a fully equivalent orbital by rotation about that axis. For octahedral complexes the orbital angular momentum is absent for $A_{1g}$, $A_{2g}$ and $E_g$ term, but can be present for $T_{1g}$ and $T_{2g}$ terms. Magnetic moments of the complex ions with $A_{2g}$ and $E_g$ ground terms may depart from the spin-only value by a small amount. The magnetic moments of the complexes possessing T ground terms usually differ from the high spin value and vary with temperature. The magnetic moments of the complexes having a $^6A_{1g}$ ground term are very close to the spin-only value and are independent of the temperature.

For octahedral and tetrahedral complexes in which spin-orbit coupling causes a split in the ground state an orbital moment contribution is expected. Even no splitting of the ground state appears in cases having no orbital moment contribution, an interaction with higher states can appear due to spin-orbit coupling giving an orbital moment contribution.

Practically the magnetic moment value of the unknown complex is obtained on Gouy Magnetic balance. Faraday method can also be applied for the magnetic susceptibility measurement of small quantity of solid samples.

The gram susceptibility is measured by the following formula:

$$\chi_g = \frac{\Delta W}{W} \cdot \frac{W_{std}}{\Delta W_{std}} \cdot \chi_{std}$$

Where $\chi_g$ = Gram Susceptibility

$\Delta W$ = Change in weight of the unknown sample with magnet on and off.

W = Weight of the known sample

$\Delta W_{std}$ = Change in weight of standard sample with magnets on and off.

$W_{std}$ = Weight of standard sample.

$\chi_{std}$ = Gram susceptibility of the standard sample.

## 2.1.6 CONDUCTIVITY

The resistance of a sample of an electrolytic solution is defined by

$$R = \rho\,[\,l/A]$$

Where, l is the length of a sample of electrolyte and A is the cross sectional area. The symbol $\rho$ is the proportionality constant and is a property of a solution.

This property is called resistivity or specific resistance. The reciprocal of resistivity is called conductivity, $\kappa$

$$\kappa = l/\rho = l/RA$$

Since l is in cm, A is in $cm^2$ and R in ohms ($\Omega$), the units of $\kappa$ are $\Omega^{-1}\,cm^{-1}$ or S $cm^{-1}$ (Siemens per cm).

**Molar Conductivity**

If the conductivity κ is in $\Omega^{-1}$ $cm^{-1}$ and the concentration C is in mol $cm^{-3}$, then the molar conductivity Λ is in $\Omega^{-1}$ $cm^2$ $mol^{-1}$ and is defined by:

$$\Lambda = \kappa/C$$

Where, C is the concentration of solute in mol $cm^{-3}$.

Conventionally solutions of $10^{-3}$ M concentration are used for the conductance measurement. Molar conductance values of different types of electrolytes in a few solvents are given below:

A 1:1 electrolyte may have a value of 70-95 $ohm^{-1}$ $cm^2$ $mol^{-1}$ in nitromethane, 50-75 $ohm^{-1}$ $cm^2$ $mol^{-1}$ in dimethyl formamide and 100-160 $ohm^{-1}$ $cm^2$ $mol^{-1}$ in methyl cyanide. Similarly a solution of 2:1 electrolyte may have a value of 150-180 $ohm^{-1}$ $cm^2$ $mol^{-1}$ in nitromethane, 130-170 $ohm^{-1}$ $cm^2$ $mol^{-1}$ in dimethylformamide and 140-220 $ohm^{-1}$ $cm^2$ $mol^{-1}$ in methyl cyanide[9-11].

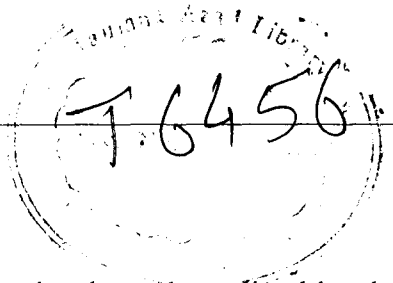
## 2.1.7 MASS SPECTROMETRY

In mass spectrometry, a substance is bombarded with an electron beam having sufficient energy to fragment the molecule. The positive fragments which are produced (cations and radical cations) are accelerated in a vacuum through a magnetic field and are sorted on the basis of mass-to-charge ratio. Since the bulk of the ions produced in the mass spectrometer carry a unit positive charge,

the value m/e is equivalent to the molecular weight of the fragment. The analysis of mass spectroscopy information involves the re-assembling of fragments, working backwards to generate the original molecule.

A very low concentration of sample molecules is allowed to leak into the ionization chamber (which is under a very high vacuum) where they are bombarded by a high-energy electron beam. The molecules fragment and the positive ions produced are accelerated through a charged array into an analyzing tube. The path of the charged molecules is bent by an applied magnetic field. Ions having low mass (low momentum) will be deflected most by this field and will collide with the walls of the analyzer. Likewise, high momentum ions will not be deflected enough and will also collide with the analyzer wall. Ions having the proper mass-to-charge ratio, however, will follow the path of the analyzer, exit through the slit and collide with the collector. This generates an electric current, which is then amplified and detected. By varying the strength of the magnetic field, the mass-to-charge ratio which is analyzed can be continuously varied.

The output of the mass spectrometer shows a plot of relative intensity vs the mass-to-charge ratio (m/e). The most intense peak in the spectrum is termed the base peak and all others are reported relative to it's intensity. The peaks themselves are typically very sharp, and are often simply represented as vertical



lines. The process of fragmentation follows simple and predictable chemical pathways and the ions, which are formed, will reflect the most stable cations and radical cations, which that molecule can form. The highest molecular weight peak observed in a spectrum will typically represent the parent molecule, minus an electron, and is termed the molecular ion ($M^+$). Generally, small peaks are also observed above the calculated molecular weight due to the natural isotopic abundance of $^{13}C$, $^{2}H$, etc. Many molecules with especially labile protons do not display molecular ions, an example of this is alcohols, where the highest molecular weight peak occurs at m/e one less than the molecular ion (M-1). Fragments can be identified by their mass-to-charge ratio, but it is often more informative to identify them by the mass which has been lost. That is, loss of a methyl group will generate a peak at M-15; loss of an ethyl, M-29, etc

## 2.1.8 ELEMENTAL ANALYSES

The chemical analysis is quite helpful in fixing the stoichiometric composition of the ligand as well as its metal complexes. Carbon, hydrogen and nitrogen analyses were carried out on a Perkin Elmer-2400 analyzer. Chloride was analyzed by conventional method[12]. For the metal estimation[13], a known amount of complex was decomposed with a mixture of nitric, perchloric and sulfuric acids in a beaker. It was then dissolved in water and made up to known

volume so as to titrate it with standard EDTA. For chloride estimation, a known amount of the sample was decomposed in a platinum crucible and dissolved in water with a little concentrated nitric acid. The solution was then treated with silver nitrate solution. The precipitate was then dried and weighed.

### 2.1.9 JOB'S METHOD

Job's method of continuous variation is commonly used procedure for determining the composition of the complexes in solution[14]. Job's method, as commonly practiced, is carried out in batch modes by mixing aliquots of two equimolar stock solutions of the metal and the ligand. These solutions are prepared in a manner such that the total analytical concentration of the metal and ligand is maintained constant, while the ligand: metal ratio varies from flask to flask, that is:

$$C_M + C_L = k$$

Where $C_M$ and $C_L$ are analytical concentration of the metal and the ligand, respectively and k is the constant. The absorbance is plotted as a function of mole fraction (X) of the ligand or metal in the flasks.

Where, $X = X_L \text{ or } X_M$

$$X_L = C_L / C_M + C_L$$

$X_L$ is the mole fraction of the ligand and $X_M$ is the mole fraction of the metal.

The resulting curves, called as Job's plot, yield a maximum (or a minimum) the position of which indicates the metal: ligand ratio of the complex in solution. For example a maximum corresponding to 0.5 on the mole ratio fraction of the ligand scale suggest a complex of 1:1 composition, while a maxima at 0.67 and 0.75 indicate complexes of 2:1 and 3:1 stiochiometry, respectively.

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# CHAPTER-3

# Synthesis and spectral studies of 12-membered tetraimine macrocyclic ligand and its complexes

## 3.1 INTRODUCTION

Macrocyclic complexes are extensively studied from the viewpoint of molecular recognition, artificial catalyst and supramolecular structures[1]. Macrocyclic ligands form metal complexes, which in general are more stable than the complexes with analogous open chain ligands (Macrocyclic effect)[2]. Macrocyclic ligands have long been employed as selective host for a wide variety of guest molecules and ions. The recognition of a metal ion by a macrocyclic ligand and modification of the properties of resulting complex is closely related to metal ion size compatibility with the ligand cavity[3]. The high selectivity and strong coordination ability of the macrocyclic ligand toward transition metal ions have attracted considerable attention because of the wide range of applications they have in which they act as a model mimicking naturally occurring metalloprotiens[4] and metalloenzymes, as electron carriers in redox reactions[5], as dioxygen carriers[6], as ionophores in a number of biochemical processes[7,8], as antitumor drugs[9], as MRI contrast agents[10] and in radiopharmaceutical chemistry[11]. Condensation between dicarbonyl and diamine has played a vital role in the development of synthetic macrocyclic ligands, which have been proved to be fruitful source of tetraazamacrocycles[12,13]. In view of the fact that for specific dicarbonyl and diamine precursors, the structure of the condensation product can be

conditioned by controlling the reaction condition, thus [1+1], [1+2] and [2+2] condensation reaction lead to the formation of open chain and cyclic structures by selecting appropriate solvent, pH, temperature and the type of metal ion[14]. Macrocycles, especially one's containing aromatic moieties, are known to form charge transfer complexes with a variety of guests. These macrocycles were used to study the complexation of diverse guests so as to provide new insight into non-covalent bonding interactions, chiefly cation π-interaction, which involves the stabilization of the positive charge by the face of an aromatic ring[15]. A variety of Schiff base macrocyclic complexes derived from dicarbonyl and diamine precursors have been reported from our laboratory[16-18]. Very few macrocycles have been synthesized by the condensation reaction between benzil and diamine subunits[19-20]. In view of the fact that the formation of Schiff base macrocycles from aromatic amines is slow enough, reactions can proceed, resulting in high yields of [2+2] macrocycles[21]. Therefore, efforts have been made to prepare a macrocyclic ligand, (L): 5,6;11;12-dibenzo-phenone-2,3;8,9-tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene by the condensation of 3,4-diaminobenzophenone and benzil and to study its interaction with Fe(III), Co(II) and Cu(II) ions, with a view of exploring the coordinating capability of the ligand to encapsulate metal ions and to examine the probable structure, mode of bonding, magnetic and spectroscopic properties.

## 3.1.2 EXPERIMENTAL

### Materials and Methods

Metal salts, $FeCl_3$ anhydrous, $CoCl_2.6H_2O$ and $CuCl_2.2H_2O$ (E. Merck) were commercially available pure samples. Benzil (BDH) and 3,4-diamino-benzophenone (Fluka) were used as received. Methanol used as solvent was dried by the standard method[22].

**Synthesis of macrocyclic ligand, (L)**

**2,3;8,9-dibenzophenone-5,6;11,12-tetraphenyl-1,4,7,10-tetraazacyclodo-deca-1,3,7,9-tetraene.**

A methanolic solution (25 $cm^3$) of 3,4-diaminobenzophenone (0.850 g, 4 mmol) was slowly added over a period of 2 h into a solution of benzil (0.84 g, 4 mmol) dissolved in 25 $cm^3$ of methanol with constant stirring in 1:1 molar ratio. The solution was refluxed and stirred for 12 h. The reaction mixture was then kept for evaporation resulting in a yellow solid product on standing for about 48 h. The product was filtered, washed several times with methanol and vacuum dried. m.p.140°C. Elemental analyses Found (Calcd.) for $C_{54}H_{36}N_4O_2$ (772.90): C, 84.70(83.90); H, 4.70(4.70); N, 7.42(7.24).

**Synthesis of the complexes.**

**Dichloro[2,3;8,9-dibenzophenone-5,6;11,12-tetraphenyl-1,4,7,10-tetraaza-cyclododeca-1,3,7,9-tetraene] iron(III)chloride and metal(II) [M=Co and Cu]**

Equimolar amounts of $FeCl_3$ anhydrous, $CoCl_2.6H_2O$ or $CuCl_2.2H_2O$ (1 mmol) in methanol (25 $cm^3$) and the ligand, (L) (1 mmol) taken in MeOH (25 $cm^3$) were reacted under reflux condition followed by stirring for ca.15 h. The reaction mixture thus obtained was continually evaporated leading to the isolation of microcrystalline products. The product thus formed was filtered, washed several times with methanol and dried in vacuo.

### 3.1.3 Physical Measurements

The FAB mass spectrum recorded on Jeol SX 102 mass spectrometer using m-nitrobenzylalcohol as matrix solvent unless otherwise stated, elemental analyses were determined with a Perkin Elmer-2400 C,H,N analyzer and $^1H$ NMR spectra was obtained in $d_6$-DMSO using a Bruker AC 200E NMR spectrometer with $Me_4Si$ as internal standard, at the microanalytical laboratory CDRI, Lucknow, India. The electronic spectra in DMSO were recorded on Pye-Unicam-8800 spectrophotometer at room temperature. The FT-IR spectra (4000-200 $cm^{-1}$) of the complexes were recorded as KBr/CsI pellets on a Perkin Elmer-2400 spectrophotometer. Metals and chlorides were determined

volumetrically[23] and gravimetrically[22], respectively. The conductivities of $10^{-3}$ M solution of the complexes in DMSO were obtained on a systronic type 302 digital conductivity meter equilibrated at 25 ± 0.1°C. Magnetic susceptibility measurements were made at room temperature on a Faraday balance. Spectroscopic measurements (Job's method) were performed at room temperature on an Elico SL 159 spectrophotometer.

### 3.1.4 RESULTS AND DISCUSSION

A tetraimine Schiff base macrocyclic ligand, (L) has been prepared by the condensation between benzil and 3,4-diaminobenzophenone (1:1 molar ratio) in methanol as shown in **Figure 1**. The level of the purity of the ligand was checked by T.L.C on silica gel-coated plates. The T.L.C of the ligand, (L) reveals the presence of both [1+1] and [2+2] condensation product. The [1+1] condensation product (crude yield: < 25%) and [2+2] condensation product (crude yield: > 60%) were separated as minor and major condensation products, respectively. The [2+2] condensation product was recrystallized from methanol resulting in a pale yellow microcrystalline product (m.p. 140-142°C) and was characterized on the basis of the results of elemental analyses, FAB-mass, IR and $^{1}$H NMR spectroscopy. The FAB mass spectrum recorded at room temperature of the metal free ligand, L confirms the proposed formula by showing a peak at m/z 773 corresponding to the macrocyclic moiety,

$[(C_{54}H_{36}N_4O_2)^+$, calcd. atomic mass 772.904 a.m.u]. Complexation reactions between the ligand, (L) and the metal salts were carried out to investigate the coordination capability of the ligand, (L). The complexes were prepared by reaction of the ligand, (L) with appropriate metal salts in 1:1 molar ratios in methanol. The purity of the complexes was also checked by T.L.C method. Analytical data **(Table 1)** of these complexes correspond to the formation of mononuclear complexes of the type, $[FeLCl_2]Cl$ and $[MLCl_2]$ M = Co(II) and Cu(II). The ligand and the complexes formed as solids stay stable in atmosphere and dissolve in solvents DMSO, MeCN and MeOH. The molar conductance data of the $10^{-3}$ M solutions of the complexes measured in DMSO indicate the non-electrolytic nature [23] of Co(II) and Cu(II), while that for the Fe(III) complex corresponds to a 1:1 electrolyte[24]. The composition of the complexes has been analyzed using Job's method[25], where a maximum corresponding to 0.5 on the mole ratio fraction of the ligand scale suggests that the above-mentioned complexes have 1:1 composition. A single crystal could not be obtained for both ligand and the complexes, even after inordinate attempts suitable for X-ray crstallography. However, the analytical, spectroscopic and magnetic data enable us to predict the possible structure shown in **Figure 1 and 2.**

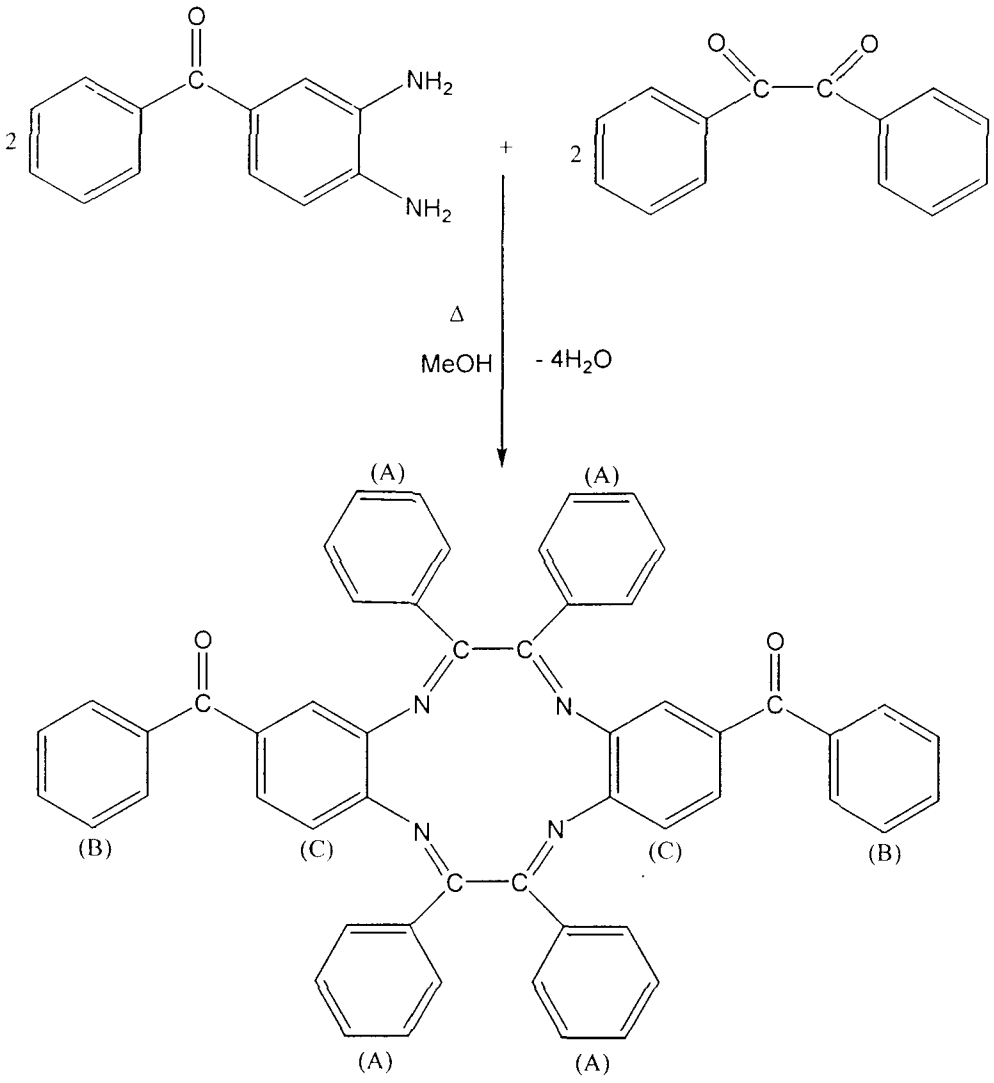


**Figure 1**. Preparation and structure of ligand (L).

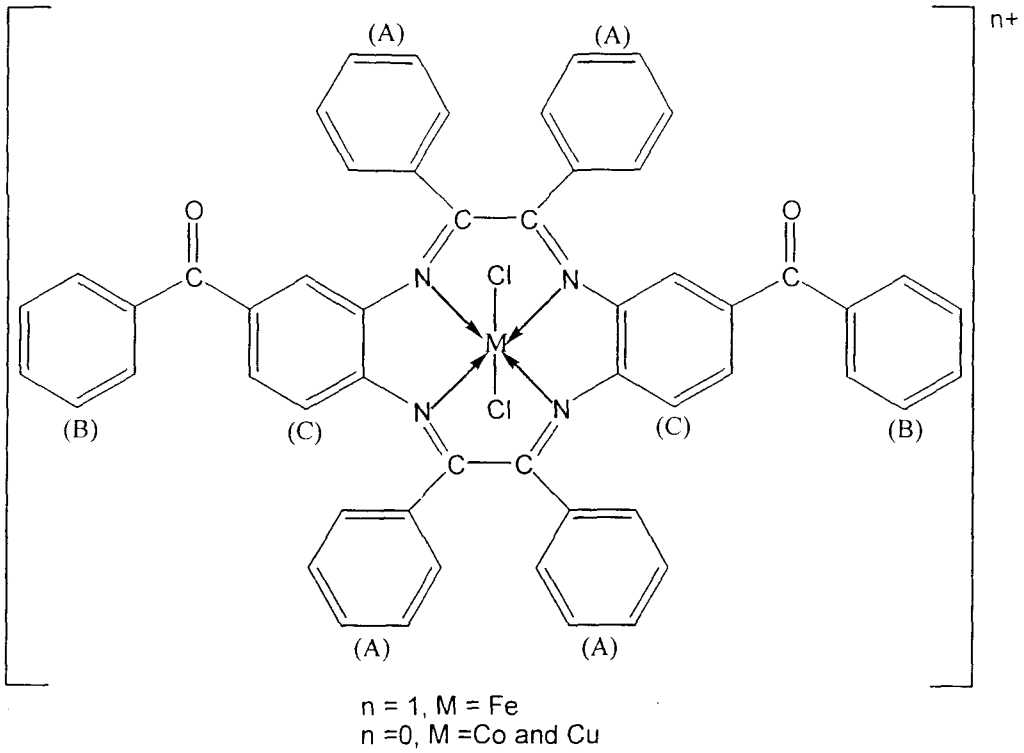


**Figure 2**. Suggested structure of macrocyclic complexes

**Table 1: Physical and analytical data of the ligand and its complexes.**

| Compounds | F.W. (Calc.) | Color | M.P (°C) | Yield (%) | Found (Calc.) % | | | | | Molar Conductance ($cm^2\Omega^{-1}mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | M | Cl | |
| Ligand (L) | 772.90 | Pale Yellow | 140 | >60 | 84.70 (83.91) | 4.70 (4.70) | 7.42 (7.24) | - | - | - |
| $[FeLCl_2]Cl$ | 935.10 | Wine red | 231 | 58 | 69.00 (69.40) | 3.80 (3.90) | 5.94 (6.00) | 6.00 (6.00) | 11.30 (11.40) | 68 |
| $[CoLCl_2]$ | 902.74 | Brown | 220 | 63 | 70.90 (71.80) | 4.00 (4.09) | 6.00 (6.20) | 6.32 (6.50) | 7.40 (7.90) | 20 |
| $[CuLCl_2]$ | 907.40 | Dark Brown | 205 | 69 | 71.00 (71.50) | 3.80 (4.00) | 6.14 (6.20) | 7.14 (7.00) | 7.22 (7.81) | 23 |

### 3.1.5 FT-IR SPECTRA

The IR spectra (4000-200 $cm^{-1}$) of both ligand and the complexes feature absorption bands characteristics of various functional groups of macrocyclic moiety providing information regarding the formation of macrocyclic ligand and its coordination mode in the complexes. The relevant ir bands with their possible assignments are shown in **Table 2**. In order to avoid the obvious confusion between the absorption bands corresponding to the carbonyl group of 3,4-diaminobenzophenone and benzil in condensed product, the ir spectrum of the ligand has been compared with regard to the ir spectra of 3,4-diaminobenzophenone and benzil. The formation of the macrocyclic ligand has been confirmed by the appearance of the ν(C=N) band[26] at 1625 $cm^{-1}$ and the absence of the ν($NH_2$) band at 3400 $cm^{-1}$ indicating that Schiff base condensation between carbonyl groups of benzil and amino groups of 3,4-diaminobenzophenone has taken place. A significant negative shift in ν(C=N) stretching mode appearing in 1580–1560 $cm^{-1}$ region for the complexes as compared to free ligand suggest the involvement of imine nitrogens of the (C=N) groups in coordination with metal ions[27,28]. Moreover two sharp distinct bands in the regions 333–320 $cm^{-1}$ and 450–420 $cm^{-1}$ were assigned to ν(M-Cl) and ν(M-N), respectively which provide compelling evidence for the

coordinated metal ion in the ligand framework[29,30]. The other absorption peaks corresponding to aromatic ν(C-H) and ν(C=C) appear at their proper positions.

### 3.1.6 Electronic spectra

The electronic spectrum of Fe (III) complex displays three bands at 18,000, 20,000 and 23,120 $cm^{-1}$ **(Table 3)** which may be assigned to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4A_{1g}$, $^4E_g$ transitions, respectively typical of an octahedral geometry[31]. The observed magnetic moment of $[FeLCl_2]Cl$ (5.86 B.M) corresponds to a high spin octahedral Fe(III) complex. The visible spectrum of Co(II) complex shows two bands discerned at 8,800 and 17,850 which may reasonably be assigned to the transitions $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$, respectively indicating distorted octahedral geometry with $D_4h$ symmetry[32,33]. This has been further corroborated by the observed magnetic moment of 4.91 B.M. The electronic spectrum of the six-coordinated Cu(II) complex having either $D_{4h}$ or $C_{4v}$ symmetry and the $E_g$ and $T_{2g}$ levels of $^2D$ free ion will split into $B_{1g}$, $A_{1g}$, $B_{2g}$ and $E_g$ levels, respectively. Thus three spin allowed transitions are expected in the visible and in the near IR regions, but only a few complexes are known, in which such bands are resolved either by "Gaussian analysis" or by "Single crystal polarization" studies[34]. These bands have been assigned as $^2B_{1g} \rightarrow {}^2A_{1g}$ $(d_{x^2-y^2} - d_{z^2})$, $^2B_{1g} \rightarrow {}^2B_{2g}$ $(d_{x^2-y^2} - d_{xy})$ and $^2B_{1g} \rightarrow {}^2E_g$ $(d_{x^2-y^2} - d_{xz,yz})$ transitions in the increasing order of their energies. The energy level sequence will depend on the amount of tetragonal distortion

**Table 2: IR Spectral data of the ligand and its complexes ($cm^{-1}$).**

| Compounds | ν(C=N) | ν (C=O) | ν (M-N) | ν (M-Cl) | ν ($C_6H_5$) | |
|---|---|---|---|---|---|---|
| | | | | | ν (C-H) | ν (C=C) |
| Ligand (L) | 1625 | 1670 | - | - | 3008 | 1595 |
| $[FeLCl_2]Cl$ | 1580 | 1661 | 420 | 333 | 3000 | 1590 |
| $[CoLCl_2]$ | 1585 | 1666 | 450 | 330 | 3010 | 1595 |
| $[CuLCl_2]$ | 1560 | 1660 | 444 | 320 | 3005 | 1596 |

**Table 3: Magnetic moments (B. M) and electronic spectral data ($cm^{-1}$) of the macrocyclic complexes with their assignments.**

| Complexes | $\mu_{eff}$ B.M | Band position ($cm^{-1}$) | Assignments |
|---|---|---|---|
| $[FeLCl_2]Cl$ | 5.86 | 18,000 | $^6A_1g \rightarrow {}^4T_1g$ |
| | | 20,000 | $^6A_1g \rightarrow {}^4T_2g$ |
| | | 23,120 | $^6A_1g \rightarrow {}^4A_1g, {}^4Eg$ |
| $[CoLCl_2]$ | 4.55 | 8,800 | $^4T_1g(F) \rightarrow {}^4T_2g(F)$ |
| | | 17,850 | $^4T_1g(F) \rightarrow {}^4A_2g(F)$ |
| $[CuLCl_2]$ | 1.90 | 13,750 | $^2B_1g \rightarrow {}^2A_2g$ |
| | | 16,750 | $^2B_1g \rightarrow {}^2Eg$ |

due to ligand field and Jahn-teller effect[35,36]. The spectrum of Cu(II) complex reported here show two characteristic bands at 13750 and 16750 $cm^{-1}$ which may reasonably be assigned to $^2B_{1g} \rightarrow {}^2A_{1g}$ and $^2B_{1g} \rightarrow {}^2E_g$ transitions, respectively. The band corresponding to $^2B_{1g} \rightarrow {}^2B_{2g}$ transition was not observed as a separate band, which may be due to tetragonal distortion [36]. The observed magnetic moment of (1.90 B.M) further supplements the electronic spectral data.

### 3.1.7 $^1$H NMR spectrum

NMR Spectrum of the ligand, L **(Figure 3)** recorded in $d_6$-DMSO at room temperature confirms the integrity of the ligand framework. The spectrum of the ligand shows signals in the range of 7.31-8.32 ppm indicating the presence of ring protons. In order to differentiate the aromatic ring protons the symbols (A), (B) and (C) have been assigned. The spectrum exhibit a multiplet in the region 7.31-7.50 ppm which may be assigned to[20] aromatic ring protons(A) (m, 20H). Multiplets in the region 7.60-7.83 ppm may be assigned to phenyl protons(B) (m, 10H)[37]. However, a multiplet in the 8.18-8.32 ppm region may be assigned to the ring protons(C) (m, 6H)[37]. The $^1$H NMR spectrum does not show any peak corresponding to $NH_2$ of the uncondensed 3,4-diaminobenzophenone moiety, which further supports the formation of the macrocyclic ligand.

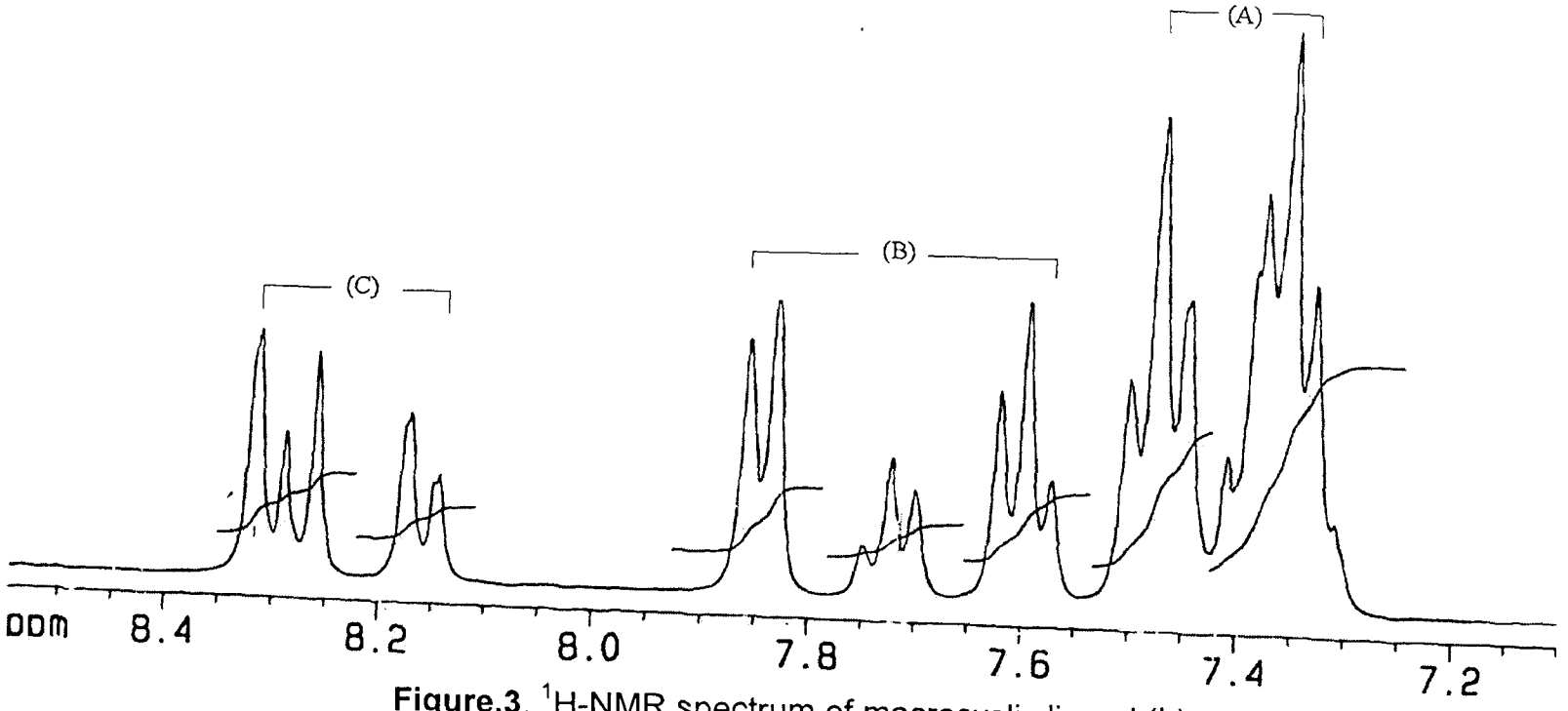


**Figure.3**. $^{1}$H-NMR spectrum of macrocyclic ligand (L)

### 3.1.8 Job's plot

Job's method of continuous variation is commonly used for determining the composition of the complex in solution. These solutions were prepared in a manner that the total analytical concentration of the metal and ligand remains constant, while the ligand: metal ratio varies from flask to flask, that is:

$$C_M + C_L = k$$

Where $C_M$ and $C_L$ are analytical concentration of the metal and the ligand, respectively and k is the constant. The absorbance is plotted as a function of mole fraction (X) of the ligand or metal in the flasks. The resulting curve is known as Job's plot.

$$\text{Where, } X = X_L \text{ or } X_M$$

$$X_L = C_L / C_M + C_L$$

$X_L$ is the mole fraction of the ligand and $X_M$ is the mole fraction of the metal.

The Job diagram **(Figure 4)** obtained for iron(III), cobalt(II) and copper(II) complexes at $\lambda$ = 490, 500 and 645 nm respectively, intersect at X = 0.5, suggesting 1:1 stoichiometry of each complex. The same profile was observed when the diagrams were constructed at different wavelengths.

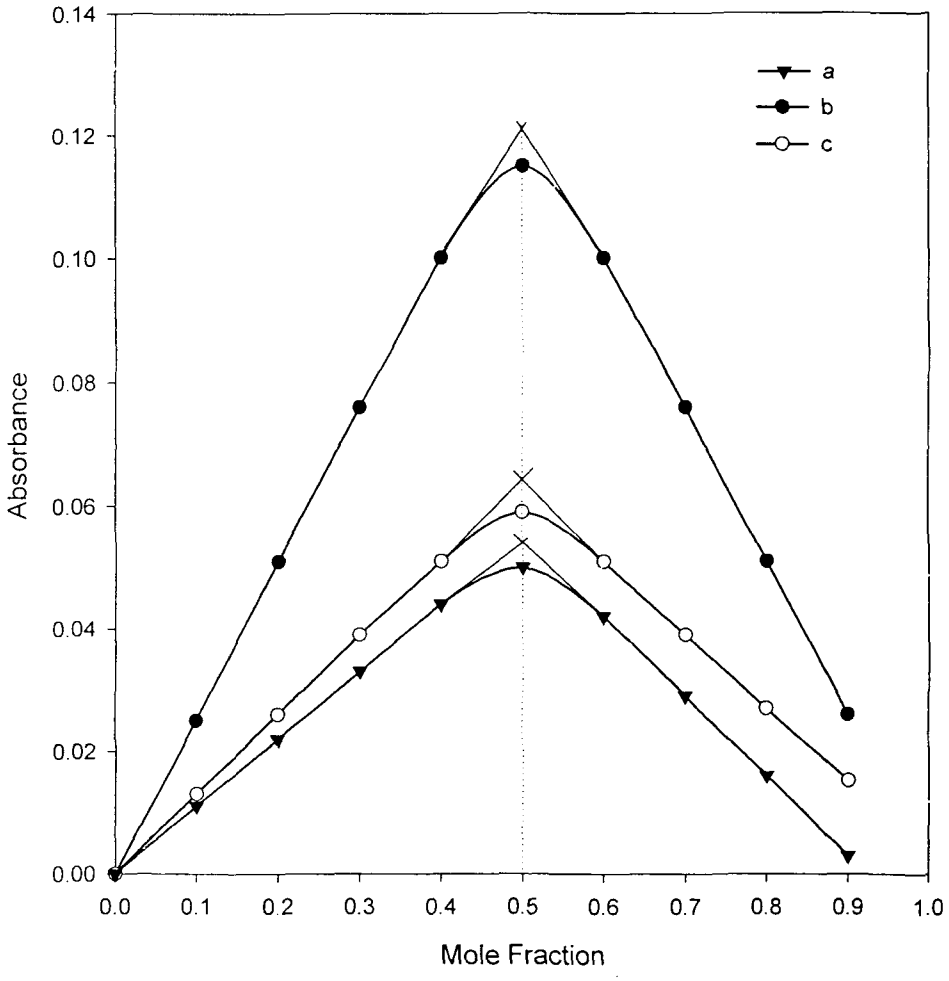


**Figure.4**. Job's plots
(a) Fe(III) complex at 490 nm
(b) Co(II) complex at 500 nm
(c) Cu(II) complex at 645 nm

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# CHAPTER-4

# Metal-ion directed synthesis and characterization of tetraimine macrocyclic complexes derived from 9,10-phenanthrenequinone and 1,2-diaminoethane

## 4.1 INTRODUCTION

The design and synthesis of polyazamacrocyclic ligands and their complexes have accelerated research interest in the recent past due to their unique coordination chemistry[1-3]. The structural, thermodynamic and kinetic aspects of metal complexes with these macrocycles have been studied in detail because of their significant implications in analytical, biological and medicinal applications[4-7]. Among the polyazamacrocyclic complexes teraazamacrocylic complexes have been extensively synthesized and studied as they are known to stabilize unusual oxidation states of the coordinated metal ion[8-9] and mimic the naturally occurring metalloproteins[10]. Jeyasubramanium et. al.[11] have shown that an oxidation state such as Cu(II) could be better achieved by using an unsaturated nitrogen donor ligands rather than a saturated one, due to stabilization by $\pi$-back bonding between the metal and the nitrogens. It is a well established fact that transition metal ion act as template for the preparation of Schiff base macrocyclic complexes, which serve to direct the steric course of the reaction preferentially towards cyclic rather than the oligomeric products[12]. Several Schiff base macrocyclic complexes have been synthesized by the condensation of aromatic ketones or aldehydes with aromatic and aliphatic primary diamines[13-15]. S. Chandra et. al.[16] have synthesized 12-membered Schiff base macrocyclic complexes derived from aromatic diketone (Benzil)

and 1,2-diaminoethane. Schiff base macrocyclic complexes bearing polyaromatic rings provide a class on the non-covalent intermolecular forces leading to multiple applications[4-7]. These non-covalent molecular interactions, chiefly cation-π interactions make a significant contribution to the overall stability of the macrocyclic complexes. Polyaromatic compounds containing three or more rings behave as strong π- donors owing to their electron rich and polarizable π- system[17]. Literature survey reveals that many acyclic complexes of polyaromatic compounds have been synthesized and studied. Giangiacomo and Dutton[18] showed in their reconstitution experiment, using 9,10-phenanthrenequinone that o-quinones can serve as electron acceptors in native system without changes in the functionality of the photosystem. Recently, Rh(III) complex of 9,10-phenanthrenequinone has been reported[19] which promotes the direct DNA cleavage and photoxidation. Phenanthrenequinones have also been used as pendant groups in porphyrin ring which serve as a biomemitic model for the electron transfer[20]. In view of the aforesaid application it was thought worthwhile to synthesize and characterize tetraimine macrocyclic complexes bearing polyaromatic rings derived from the template condensation of 9,10-phenanthrenequinone and 1,2-diaminoethane.

## 4.1.2 EXPERIMENTAL

### Materials and Method

The metal salts $MnX_2.4H_2O$ (X = Cl and $NO_3$), $FeX_2.nH_2O$ (n = 2 and 6; X = Cl and $NO_3$), $MX_2.6H_2O$ ($Co^{2+}$ and $Ni^{2+}$; X = Cl and $NO_3$), $CuX_2.nH_2O$ (n = 2 and 3; X = Cl and $NO_3$) respectively, $ZnCl_2$, $Zn(NO_3)_2.6H_2O$, (All E. Merck) were commercially available as pure samples. The chemicals 1,2-diamioethane and 9,10-phenanthrenequinone (E. Merck) were used as received. Methanol used as a solvent, was distilled and dried before use by conventional method[21].

**Synthesis of dichloro/dinitrato (2,3;8,9-diphenanthrene-1,4,7,10-tetra-iminecyclododecane) metal(II) [$MLX_2$]; (M = Mn(II), Fe(II), Co(II), Ni(II) and Zn(II); X = Cl and $NO_3$).**

A methanolic solution (30 $cm^3$) of 1,2-diaminoethane (6 mmol, 0.39 ml) was added to a metal salt (3 mmol) solution prepared in 20 $cm^3$ methanol. The reaction mixture was stirred for 1h resulting in color change. To this reaction mixture was added a MeOH solution (30 $cm^3$) of 9,10-phenanthrenequinone (6 mmol, 1.26g). The resulting reaction mixture was than refluxed for 7h leading to the isolation of colored solid product. The product was filtered off, washed several times with methanol and dried in vacuum at room temperature.

**Synthesis of (2,3;8,9-diphenanthrene-1,4,7,10-tetraiminecyclododecane) Copper(II)chloride or nitrate $[CuL]X_2$ (X = Cl and $NO_3$)**

The procedure was exactly analogous to the previous one except that $CuX_2.nH_2O$ (n = 2, 3; X = Cl and $NO_3$) respectively, was used.

**Antimicrobial activity**

The antimicrobial activity of the compounds was tested against C. albicans and E. Coli $K_{12}$. The holes of 1mm diameter were punched in the respective agar plates. The fresh stock solutions of the compounds were prepared by dissolving them in DMSO, to obtain a concentration of 5mg/ml for Ni(II) and Co(II) and Fe(II) complexes. DMSO alone was taken as a control.

### 4.1.3 Physical measurements

Elemental analyses were obtained from microanalytical laboratory, using Perkin-Elmer-2400 C,H,N analyzer. Analytical thin layer chromatography was performed on silica gel coated glass plates using ethylacetate (85%), methanol (10%) and acetic acid (5%) as eluent. Infrared spectra were recorded on a Perkin-Elmer-2400 spectrophotometer at room temperature with KBr/CsI pellets. $^1H$ NMR and $^{13}C$ spectra were recorded in DMSO-$d_6$ using a Bruker DRX-300 spectrometer and JEOL Eclipse-400 spectrometer, respectively. EPR spectra were recorded on JEOL JES RE2X EPR spectrometer. Metals and chlorides were determined volumetrically[22] and gravimetrically[23]. The molar

conductivities of the $10^{-3}$ M solutions in DMSO were obtained on a systronics type 302 conductivity bridge equilibrated at 25 ± 0.1°C. Magnetic susceptibility measurements were carried out using a faraday balance at 25°C. The antimicrobial activity of the Fe(II), Ni(II) and Cu(II) complexes were tested against C. albicans and E. Coli $K_{12}$ by agar well diffusion method. The bacterial strain of E. Coli $K_{12}$ and the fungal strain of C. albicans (J.N.M.C 1520) used in this study were procured from Jawaharlal Nehru Medical College Microbiology centre. The bacterial strain was grown on the nutrient agar plate at 37°C for 16-18 h, while the fungal strain was grown on YPD agar plates at 37°C for 24-48 h.

### 4.1.4 RESULTS AND DISCUSSION

A new series of 12-membered tetraimine macrocyclic complexes of the types, $[MLX_2]$ and $[CuL]X_2$ (M = Mn(II), Fe(II), Co(II), Ni(II) and Zn(II); X = Cl and $NO_3$) **(Figure 1)** have been prepared by the template reaction of the metal salts, $MX_2.nH_2O$ or $ZnCl_2$ with 1,2-diaminoethane and 9,10-phenanthrenequinone in 1:2:2 molar ratio. The newly synthesized macrocyclic complexes have been characterized on the basis of elemental analyses, IR, $^1H$ and $^{13}C$ NMR spectra. The purity of the macrocyclic complexes was checked by TLC on silica gel coated plates, which resulted in the single spot different from starting materials.

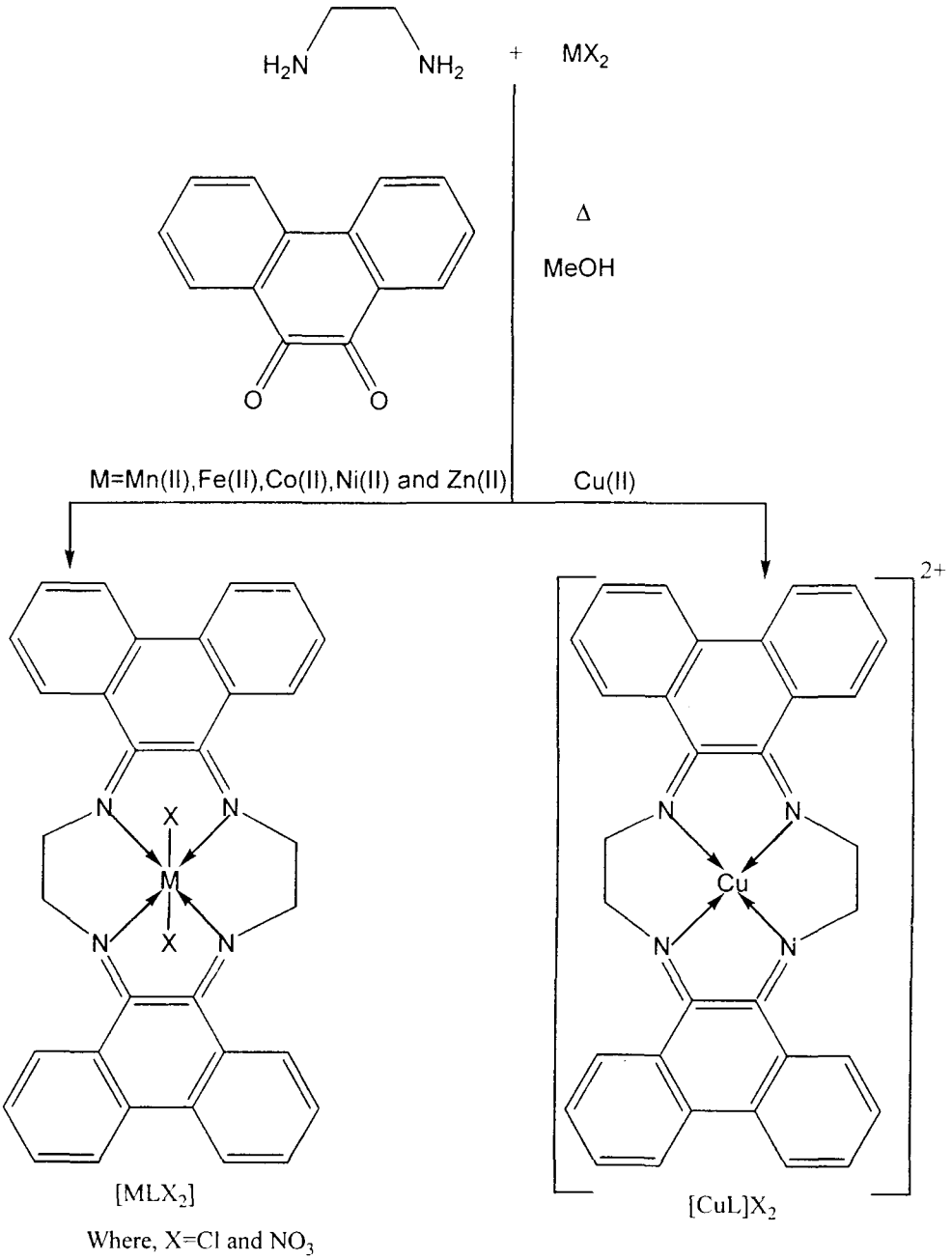



**Figure 1**. Synthesis and structure of tetraimine macrocyclic comlexes

Analytical data **(Table 1)** were found to be in accord with the proposed stoichiometry of the mononuclear complexes of the formulation $[MC_{32}H_{24}N_4X_2]$. All the complexes were found to be air stable, non-hygroscopic solids, insoluble in $H_2O$ with varying solubility in organic solvents. The molar conductance data of the $10^{-3}$ M solutions in DMSO at room temperature show non-electrolytic nature for all the complexes except for Cu(II) complexes which show 1:2 electrolytic nature[24]. All attempts to isolate the single crystals failed.

### 4.1.5 IR spectra

The IR spectra in the 4000- 200 $cm^{-1}$ range of the complexes **(Table 2)** provide information regarding the formation of the macrocyclic framework and the coordination mode in the macrocyclic complexes. The spectra show the complete absence of bands characteristic of ν(C=O) and primary amine band ν(NH) of the uncondensed 9,10-phenanthrenequinone and 1,2-diaminoethane moiety, respectively. While the appearance of a well defined absorption band in the 1595-1575 $cm^{-1}$ region attributable to[25] ν(C=N) group confirm the complete condensation of the carbonyl groups of 9,10-phenanthrenequinone moiety with amino groups of the 1,2-diaminoethane moiety. A negative shift in ν(C=N) band in the macrocyclic complexes suggests the involvement of the imine nitrogens in the formation of M–N bond[26].

**Table 1: Physical and Analytical data of the macrocyclic complexes.**

| Compounds | F.W. (Calc.) | Color | M.P (°C) | Yield (%) | Found (Calc.) % | | | | | Molar Conductance ($cm^2\Omega^{-1}mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | M | Cl | |
| $[MnLCl_2]$ | 590.41 | Dark Brown | >300 | 60 | 65.00 (65.10) | 4.69 (4.09) | 9.24 (9.48) | 9.00 (9.31) | 12.02 (12.01) | 11 |
| $[MnL(NO_3)_2]$ | 643.51 | Dark Brown | >300 | 61 | 59.33 (59.72) | 3.55 (3.76) | 13.01 (13.06) | 8.21 (8.54) | - | 16 |
| $[FeLCl_2]$ | 591.32 | Yellow | 295 | 63 | 64.36 (64.99) | 3.88 (4.09) | 8.99 (9.48) | 8.97 (9.44) | 11.37 (11.99) | 14 |
| $[FeL(NO_3)_2]$ | 644.43 | Yellow | 290 | 64 | 59.33 (59.64) | 3.66 (3.75) | 13.02 (13.04) | 8.23 (8.66) | - | 18 |
| $[CoLCl_2]$ | 594.40 | Brown | 273 | 58 | 63.84 (64.66) | 4.02 (4.07) | 9.20 (9.43) | 9.53 (9.91) | 11.85 (11.92) | 22 |
| $[CoL(NO_3)_2]$ | 647.51 | Brown | 270 | 60 | 59.00 (59.35) | 3.05 (3.74) | 12.33 (12.97) | 9.01 (9.10) | - | 20 |
| $[NiLCl_2]$ | 594.16 | Green | 286 | 65 | 64.43 (64.68) | 4.00 (4.07) | 9.35 (9.43) | 9.44 (9.88) | 11.32 (11.93) | 25 |
| $[NiL(NO_3)_2]$ | 647.27 | Green | 282 | 67 | 59.05 (59.38) | 3.33 (3.74) | 12.36 (12.98) | 8.99 (9.07) | | 28 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| $[CuL]Cl_2$ | 599.02 | Light Blue | 280 | 66 | 64.08 (64.16) | 3.99 (4.04) | 9.17 (9.35) | 10.00 (10.61) | 11.81 (11.84) | 110 |
| $[CuL](NO_3)_2$ | 652.12 | Light Blue | 276 | 65 | 58.00 (58.93) | 3.32 (3.71) | 12.66 (12.88) | 9.50 (9.74) | - | 112 |
| $[ZnLCl_2]$ | 600.85 | Pale Green | 267 | 61 | 63.78 (63.96) | 3.98 (4.03) | 9.22 (9.32) | 10.56 (10.88) | 11.68 (11.80) | 19 |
| $[ZnL(NO_3)_2]$ | 653.95 | Pale Green | 269 | 67 | 58.33 (58.73) | 3.32 (3.70) | 12.07 (12.84) | 9.78 (9.98) | - | 15 |

**Table 2: IR Spectral data of the macrocyclic complexes ($cm^{-1}$).**

| Compounds | ν(C=N) | ν (M-N) | ν (M-O) | ν (M-Cl) |
|---|---|---|---|---|
| $[MnLCl_2]$ | 1590 | 455 | - | 325 |
| $[MnL(NO_3)_2]$ | 1595 | 450 | 245 | - |
| $[FeLCl_2]$ | 1595 | 450 | - | 310 |
| $[FeL(NO_3)_2]$ | 1592 | 452 | 250 | - |
| $[CoLCl_2]$ | 1580 | 454 | - | 305 |
| $[CoL(NO_3)_2]$ | 1585 | 450 | 244 | - |
| $[NiLCl_2]$ | 1590 | 444 | - | 295 |
| $[NiL(NO_3)_2]$ | 1593 | 440 | 240 | - |
| $[CuL]Cl_2$ | 1582 | 455 | - | - |
| $[CuL](NO_3)_2$ | 1575 | 441 | - | - |
| $[ZnLCl_2]$ | 1588 | 447 | - | 290 |
| $[ZnL(NO_3)_2]$ | 1576 | 453 | 240 | - |

A further support in this regard has been obtained by the presence of a medium intensity band in the 455-440 $cm^{-1}$ region attributable to ν(M–N) vibration. The coordination of the chloro and the nitrato groups have been ascertained by the appearance of bands in 325-290 $cm^{-1}$ and 250-245 $cm^{-1}$ regions which may reasonably be assigned to ν(M–Cl) and ν(M–O) of O–$NO_2$ groups in [$MLCl_2$] and [$ML(NO_3)_2$] complexes, respectively. The spectra of the nitrato complexes also show additional bands in the 1255-1225, 1040-1025 and 888-870 $cm^{-1}$ regions, which are consistent with the monodentate coordination of the nitrate groups[27]. Absorption bands due to phenyl ring vibrations appear at their proper positions.

### 4.1.6 $^1$H NMR spectra

NMR spectra of the Zn(II) complexes recorded in DMSO-$d_6$ show three types of signals integrating two types of ring protons for the phenanthrene ring and one for the methylene proton of the condensed 1,2-diaminoethane moiety. The chemical shift (δ) values in 9.16-9.07 ppm (Ar- 8H, m), 8.80-7.87 ppm (Ar- 8H, m), regions may reasonably be assigned to phenanthrene ring protons[20] and 2.40-2.35 ppm (8H, s) region corresponds to methylene protons of condensed 1,2-diaminoethane moiety.

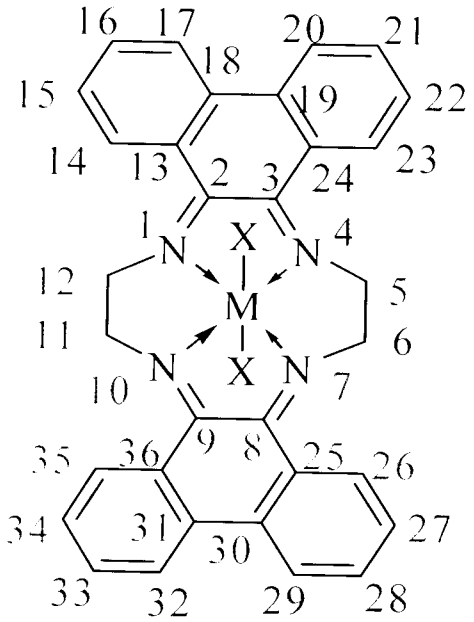
### 4.1.7 $^{13}C$ NMR spectra

The decoupled $^{13}C$ NMR spectra in DMSO- $d_6$ of the Zn(II) complexes at room temperature confirm the presence of imine, methylene and aromatic functions and in both the cases the spectra complements the assigned structure of the macrocyclic complexes **(Table 3)**.

### 4.1.8 Electronic spectra and Magnetic data

Electronic absorption spectra of the macrocyclic complexes were recorded in DMSO at room temperature. The Mn(II) complexes display three absorption bands discerned in the region 18,000-17,500, 22,500-21,454 and 26,500-25,555 $cm^{-1}$ assignable to $^6A_{1g} \rightarrow {}^4T_{1g}$, $^6A_{1g} \rightarrow {}^4T_{2g}$ and $^6A_{1g} \rightarrow {}^4E_g$, $^4A_{1g}$ transitions, respectively suggesting an octahedral geometry[28] **(Table 4)**. The observed magnetic moment values of 5.90 and 5.87 B.M close to the spin only values, further corroborate the assigned geometry[29]. Electronic spectra of Fe(II) complexes show an absorption band in the region 11,500-11,350 $cm^{-1}$ which may reasonably be assigned to $^5T_{2g} \rightarrow {}^5E_g$ transition[30]. The magnetic moment values of 5.41 and 5.30 B.M. for the Fe(II) complexes complements the electronic spectral data[31]. Visible spectra of the Co(II) complexes exhibit three bands in the regions 8,988-8,750, 14,950-14,750 and 24,545-23,578 $cm^{-1}$ corresponding to $^4T_{1g}(F) \rightarrow {}^4T_{2g}(F)$, $^4T_{1g}(F) \rightarrow {}^4A_{2g}(F)$ and $^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively indicating octahedral geometry around Co(II) ion[32].

**Table 3. $^{13}C$ NMR data of the Zn(II) macrocyclic complex**




| δ Values (ppm) | Assignments |
|---|---|
| 149.5 | $C_2$, $C_3$ and $C_8$,$C_9$ |
| 130.63 | $C_{13}$, $C_{24}$and $C_{25}$, $C_{36}$ |
| 129.01 | $C_{14}$, $C_{23}$ and $C_{26}$, $C_{35}$ |
| 128.99 | $C_{15}$, $C_{22}$ and $C_{27}$, $C_{34}$ |
| 127.06 | $C_{16}$, $C_{21}$ and $C_{28}$, $C_{33}$ |
| 124.67 | $C_{17}$, $C_{20}$ and $C_{29}$, $C_{32}$ |
| 122.14 | $C_{18}$, $C_{19}$ and $C_{30}$, $C_{31}$ |
| 65.8 | $C_5$, $C_6$ and $C_{11}$,$C_{12}$ |

**Table 4: Magnetic moments (B. M) and electronic spectral data ($cm^{-1}$) of the macrocyclic complexes.**

| Complexes | $\mu_{eff}$ B.M | Band position ($cm^{-1}$) | Assignments |
|---|---|---|---|
| $[MnLCl_2]$ | 5.90 | 18,000<br>22,500<br>26,500 | $^6A_1g \rightarrow {}^4T_1g$<br>$^6A_1g \rightarrow {}^4T_2g$<br>$^6A_1g \rightarrow {}^4Eg, {}^4A_1g$ |
| $[MnL(NO_3)_2]$ | 5.87 | 17,500<br>21,454<br>25,555 | $^6A_1g \rightarrow {}^4T_1g$<br>$^6A_1g \rightarrow {}^4T_2g$<br>$^6A_1g \rightarrow {}^4Eg, {}^4A_1g$ |
| $[FeLCl_2]$ | 5.41 | 11,500 | $^5T_2g \rightarrow {}^5Eg$ |
| $[FeL(NO_3)_2]$ | 5.30 | 11,350 | $^5T_2g \rightarrow {}^5Eg$ |
| $[CoLCl_2]$ | 4.85 | 8,988<br>14,950<br>24,545 | $^4T_1g(F) \rightarrow {}^4T_2g(F)$<br>$^4T_1g(F) \rightarrow {}^4A_2g(F)$<br>$^4T_1g(F) \rightarrow {}^4T_1g(P)$ |
| $[CoL(NO_3)_2]$ | 4.70 | 8,750<br>14,750<br>23,578 | $^4T_1g(F) \rightarrow {}^4T_2g(F)$<br>$^4T_1g(F) \rightarrow {}^4A_2g(F)$<br>$^4T_1g(F) \rightarrow {}^4T_1g(P)$ |

| | | | |
|---|---|---|---|
| $[NiLCl_2]$ | 3.16 | 8,000<br>13,600<br>26,000 | $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$<br>$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ |
| $[NiL(NO_3)_2]$ | 3.14 | 7,250<br>13,450<br>24,960 | $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$<br>$^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$<br>$^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ |
| $[CuL]Cl_2$ | 1.87 | 17,900<br>21,000 | $^2B_1g \rightarrow {}^2A_2g$<br>$^2B_1g \rightarrow {}^2Eg$ |
| $[CuL](NO_3)_2$ | 1.85 | 17,825<br>20,110 | $^2B_1g \rightarrow {}^2A_2g$<br>$^2B_1g \rightarrow {}^2Eg$ |

The observed magnetic moment values (4.85 and 4.70 B. M) were slightly higher than the spin-only value that may be explained in terms of orbital contribution expected[33] in high spin state of Co(II) ion. The Ni(II) complexes show three bands in the regions 8,000-7,250, 13,600-13,450 and 26,000-24,960 $cm^{-1}$ attributable to $^3A_{2g}(F) \rightarrow {}^3T_{2g}(F)$, $^3A_{2g}(F) \rightarrow {}^3T_{1g}(F)$ and $^3A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ transitions respectively, consistent with an octahedral environment around the Ni(II) ion[28]. The magnetic moment values of 3.16 and 3.14 B.M further corroborates the electronic spectral findings[34]. While Cu(II) complexes show two bands were observed in the visible range of 17,900-17,825 and 21,000-20,110 $cm^{-1}$ which may be assigned to the transitions $^2B_{1g} \rightarrow {}^2A_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$, respectively consistent with square planar disposition[35]. The slightly higher magnetic moment values (1.87 and 1.85 B. M) of Cu(II) complexes are consistent with an orbitally non-degenerate g-state of the Cu(II) ion[36].

### 4.1.9 E. P. R spectra

The e. p. r spectra of the powdered samples of Cu(II) complexes at room temperature exhibit a single isotropic resonance. The complexes gave $g_{\|}$ and $g_{\perp}$ values in 2.28-2.23 and 2.11-2.07 range, respectively indicating that the unpaired electron lies predominantly into the $d_{x^2-y^2}$ orbital of Cu(II) ion[37]. Proctor et.al. have postulated[38] that the magnitude of the ratio $G = (g_{\|} - 2)/(g_{\perp} - 2)$ indicates the possibility of exchange interaction in Cu(II)

complexes. The G values for the present complexes fall in the range 2.54-3.28, which indicates that G < 4. According to Hathaway[39,40], if G > 4, exchange interaction is negligible. A value of G < 4, indicates considerable exchange interaction in solid complexes. The observed "g" values are consistent with the square planar geometry around the Cu(II) ion[41].

### 4.1.10 Antimicrobial activity

The in-vitro antimicrobial activity of macrocyclic complexes $[MLCl_2]$ [M = Fe(II) and Ni(II)]and $[CuL]Cl_2$, **(Figure 2)** was carried out by agar well diffusion method as reported by the previous workers[42,43]. The antimicrobial susceptibility of these compounds against C. albicans and E. Coli $K_{12}$ were evaluated in the range of concentration between 0.5 to 5 mg/ml in each well by comparing the inhibition zone with that of the control (DMSO). Herein, we report a comparative antimicrobial screening of the macrocyclic complexes, which show maximum inhibition at a concentration 0.5 mg/ml/well (MIC). The minimum inhibitory concentration may be defined as the concentration at which there is maximum inhibition. The $[CuL]Cl_2$ complex shows a maximum inhibition of 2.4 cm ± .05 cm as revealed by the highest diameter of the inhibition zone, while the Ni(II) complex shows inhibition zone of 2.2 cm ± .05 cm as compared to that of Fe(II) complex which shows the least inhibition zone of 1.2 cm ± .05 cm. Similarly, the antibacterial activity of these compounds was

tested against E. Coli $K_{12}$. The maximum inhibitory activity was shown by Cu(II) complex, which shows an inhibition zone of 2.4 cm ± .07 cm, while Ni(II) and Fe(II) complexes show moderate inhibition zone of 1.23 ± .05 and 1.18 ± .07 cm. These complexes exhibit potential activity at the concentration dose of 0.5 mg/ml which is comparable to that of tetradentate 12-membered macrocyclic complexes, shown to have antimicrobial activity against various pathogens by disc diffusion technique[44]. The inhibitory activity of the macrocyclic complexes can be explained on the basis of chelation theory[45,46]. Chelation reduces the polarity of metal ion mainly because of partial sharing of its positive charge with the donor groups and possible electron-delocalization over the whole macrocyclic ring. This increases the lipophilic character of the macrocyclic complex, which subsequently favors the permeation of the complex through the lipid layer of the organism cell membrane and thus the normal cell processes are being impaired.

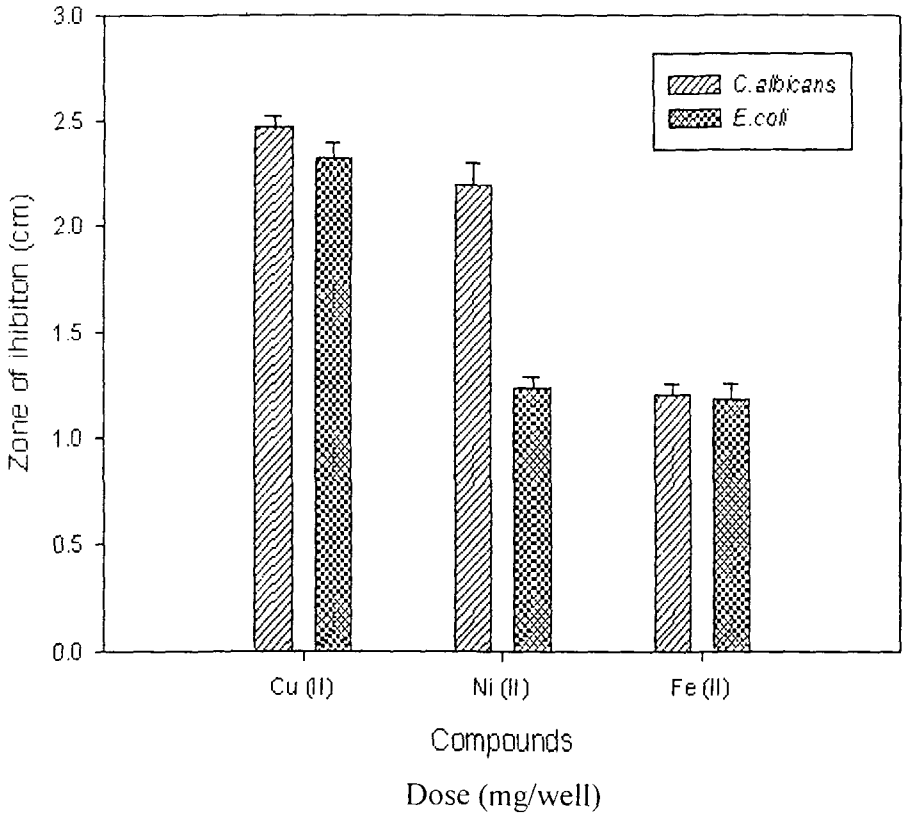



Fig 2. Antimicrobial activity of macrocyclic complexes of Cu(II), Ni(II) and Fe(II).

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# CHAPTER-5

# Synthesis and spectral studies on 16-membered diamidediimine tetraazamacrocyclic complexes, [MLCl]Cl [M=Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II)]

## 5.1 INTRODUCTION

The chemistry of naturally occurring macrocyclic complexes in general represents a vast area of research ranging over many areas of chemistry and biochemistry[1]. Tetraazamacrocycles continue to attract huge amount of research interest owing to their ability to form complexes with large range of metal ions, often with very high thermodynamic and kinetic stability with respect to metal ion dissociation[2]. Macrocyclic complexes are of significant general interest due to their varied applications[3-5] in bioinorganic chemistry, catalysis, extraction of metal ions from solutions, as dyes and pigments and the activation of small molecules give impetus to this endeavor. Since the pioneering work of Curtis[6] on the template synthesis of azamacrocycles there has been a tremendous progress in the field of polyazamacrocyclic complexes. Synthesis of macrocyclic ligands by the metal template method has been recognized as offering high yielding and selective routes to new ligands and their complexes. Lindoy and Busch[7] have described in detail the synthesis and properties of nitrogen containing macrocycles and their complexes mainly with the first row transition metal cations. Polyazamacrocyclic complexes have been studied in detail on account of their interesting stereochemistry and wide practical utility[8,9], as they have strong tendency to form stable complexes with transition metals[10]. Structural factors, such as cavity size, type and number of donor atoms

and stereochemical rigidity have been shown to play significant role in determining the binding feature of these macrocycles towards metal ions[11]. The amide macrocycles are of special interest since they can function as catalysts in many organic oxidation reactions[12,13]. An amide group offers two potential binding sites for complexation with metal cations, as in the case of o-aminobenzoic acid, which act as a bidentate ligand in which coordination occurs through the amino nitrogen and the carboxylato oxygen. However, in most of the polyamide macrocyclic complexes amide nitrogen is engaged in coordination and not the oxygen[14]. Condensation reactions between dicarbonyls and primary diamines have played an important role in the development of synthetic macrocyclic ligands, which have been proved to be fruitful source of imino macrocycles[15,16]. O-aminobenzoic acid forms complexes of 2:1 stoichiometry with a variety of divalent metal ions. These complexes have been of interest as potential inflammatory drugs, as antioxidants in films, as bond strengtheners in epoxy adhesives[17-19]. We have earlier reported[20-22] synthesis and characterization of tetraaza and hexaazamacrocyclic complexes bearing amide groups. Herein, we report metal-ion controlled synthesis and characterization of diamidediimine tetraazamacrocyclic complexes obtained from condensation reaction of o-aminobenzoic acid with o-phthalaldehyde and 1,2-diaminoethane.

## 5.1.2 EXPERIMENTAL

### Materials and method

The metal salts, $MCl_2.6H_2O$ (M = Co and Ni) $FeCl_2..2H_2O$, $CuCl_2.2H_2O$, $MnCl_2.4H_2O$, and $ZnCl_2$ (E.Merck) were commercially available as pure samples. The chemicals, o-phthalaldehyde (Fluka), 1,2-diaminoethane and o-aminobenzoic acid (E.Merck) were used as received. Methanol as a solvent was dried before use.

**Synthesis of chloro (1,2:5,6:9,10-triphenyl-11,16-dioxo-3,8,12,15-tetraaza-cyclohexadeca-3,7-diene) metal(II)chloride, [MLCl]Cl [M = Mn(II), Fe(II), Co(II), Ni(II), Cu(II)andZn (II)].**

To a methanolic solution (~25 ml) of metal chloride (2 mmols) placed in three neck flask was added a solution of o-phthalaldehyde (2 mmols, 0.27 g) at room temperature, which resulted in colour change of the reaction mixture. The contents of the reaction mixture were stirred overnight resulting in no change of its appearance. Finally methanolic solution (20 ml) of o-aminobenzoic acid (4 mmols, 0.55 g) and 1,2-diaminoethane (2 mmols, 0.13 ml) were added simultaneously and slowly to the reaction mixture, whereupon a change in color was observed. The contents of the reaction mixture were stirred for 8 h and then heated on a water bath for 4 h at 60°C leading to the isolation of solid

product. The solid product thus formed was filtered, washed several times with methanol and dried in vacuo.

### 5.1.3 Physical measurements

The results of elemental analyses were obtained from the microanalytical laboratory using a Perkin Elmer-2400 C,H,N analyzer at College of Sciences, King Saud University, Riyadh, Saudi Arabia. The IR-spectra (4000-200 $cm^{-1}$) were recorded as KBr/CsI pellets on a Perkin Elmer-2400 Spectrometer. $^1H$ NMR Spectrum was recorded in DMSO-$d_6$ at room temperature using a Bruker AC 200E NMR Spectrometer with $Me_4Si$ as an internal standard from the microanalytical laboratory, CDRI, Lucknow. Metals and chlorides were determined volumetrically[23] and gravimetrically[24] respectively. Diffuse reflectance spectra were taken on a Carl-Zeiss VSU-2P spectrophotometer using MgO as the reflectance standard. Electronic spectra in DMSO were recorded on a Pye-Unicam 8800 spectrophotometer. The electrical conductivities of $10^{-3}$ M solution in DMSO were obtained on a systronic type 302 digital conductivity meter equilibrated at 25 ± 0.1°C.

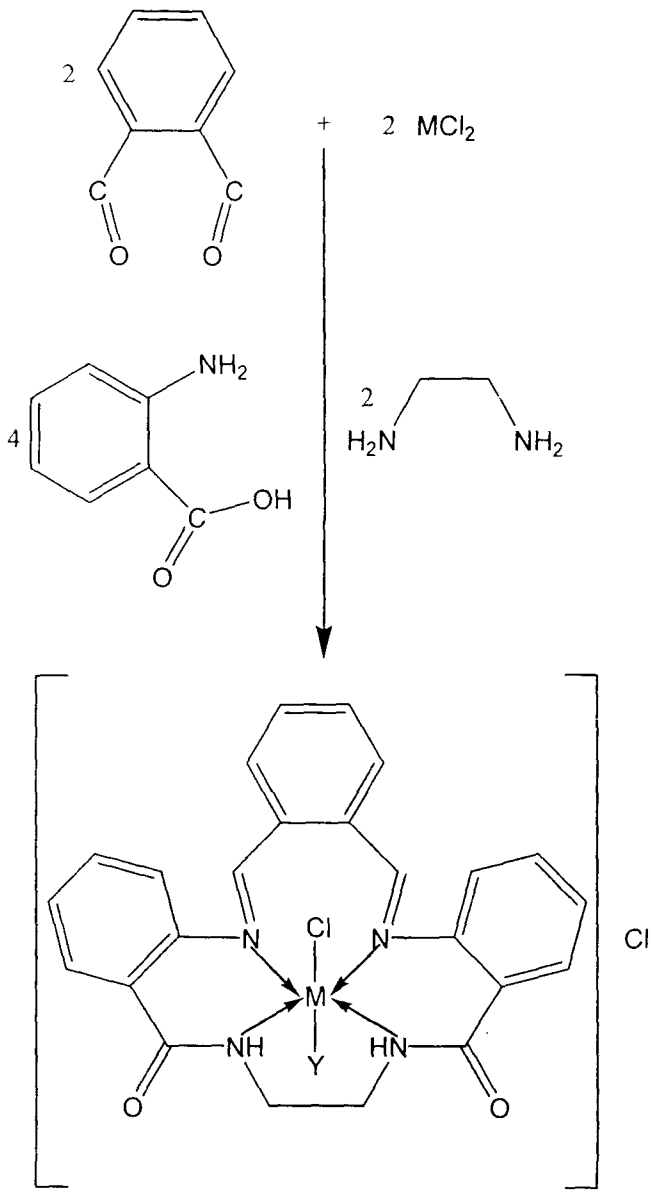
### 5.1.4 RESULTS AND DISCUSSION

A new series of tetraazamacrocyclic complexes of a few first row transition metals have been prepared via metal-promoted reaction between o-aminobenzoic acid, o-phthalaldehyde and 1,2-diaminoethane in 1:2:1:1 molar

ratio **(Figure 1)**. All the complexes have high melting points (>300°C). Elemental analyses **(Table 1)** agree well with the proposed stoichiometry of the complexes. All the complexes are stable to atmosphere and dissolve only in DMSO. The molar conductance values recorded in DMSO corresponds[25] to 1:1 electrolytic nature of the complexes.

### 5.1.5 IR spectra

The preliminary identification regarding the formation of macrocyclic complexes has been obtained from the bands seen in the IR spectra **(Table 2)**. The absence of any uncondensed primary amino and aldehydic groups reveals that the condensation has taken place. The spectra show a strong absorption band in the region 1590-1620 $cm^{-1}$ that may be assigned[26,27] to coordinated imine (C=N) stretching frequency, which supports the fact that condensation between carbonyl group of o-phthalaldehyde and amino group of o-aminobenzoic acid has taken place. All the complexes show a single sharp band appearing in the region 3200-3245 $cm,^{-1}$ attributable to coordinated secondary amino group of ethylenediamine moiety, which is found to be lower by 40-60 $cm^{-1}$ than the analogous metal free ligand[28]. In addition to it four amide bands have also been identified in the region 1700-1730, 1500-1540, 1240-1260 and 640-680 $cm^{-1}$assignable[29] to amide I [ν(C=O)], amide II [ν(C-N) + δ(N-H)], amide III [δ(N-H)] and amide IV [ϕ(C=O)] vibrations, respectively.




M =Mn(II), Fe(II), Co(II), Ni(II), Cu(II) and Zn(II); Y = DMSO

**Figure 1**

**Table 1: Physical and Analytical data of the macrocyclic complexes.**

| Compounds | F.W. (Calc.) | Color | M.P (°C) | Yield (%) | Found (Calc.) % | | | | | Molar Conductance ($cm^2\Omega^{-1}mol^{-1}$) |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | C | H | N | M | Cl | |
| [MnLCl]Cl | 522.29 | Brown | 341 | 55 | 55.03 (55.19) | 3.07 (3.86) | 10.34 (10.72) | 10.20 (10.51) | 12.89 (13.57) | 47 |
| [FeLCl]Cl | 523.20 | Yellow | 350 | 56 | 54.33 (54.09) | 3.67 (3.85) | 10.59 (10.71) | 10.33 (10.67) | 13.09 (13.55) | 53 |
| [CoLCl]Cl | 526.28 | Purple | 358 | 60 | 54.08 (54.77) | 3.42 (3.83) | 10.00 (10.64) | 11.09 (11.19) | 13.01 (13.47) | 51 |
| [NiLCl]Cl | 526.04 | Grey | 360 | 53 | 54.66 (54.79) | 3.78 (3.83) | 10.19 (10.65) | 11.04 (11.15) | 13.20 (13.48) | 59 |
| [CuLCl]Cl | 530.90 | Green | 320 | 58 | 54.06 (54.29) | 3.69 (3.79) | 10.09 (10.55) | 11.33 (11.96) | 13.14 (13.36) | 43 |
| [ZnLCl]Cl | 532.73 | Off White | 340 | 54 | 54.02 (54.11) | 3.23 (3.78) | 10.39 (10.52) | 12.11 (12.27) | 13.14 (13.30) | 49 |

**Table 2: IR Spectral data of the Ligand and its complexes ($cm^{-1}$).**

| Compounds | ν(N-H) | ν (C-H) | ν (C=N) | ν (M-N) | ν (M-Cl) | Amide Bands | | | | Ring Vibrations | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | I | II | III | IV | | | |
| [MnLCl]Cl | 3200 | 2840 | 1610 | 440 | 290 | 1710 | 1510 | 1260 | 670 | 1400 | 1080 | 725 |
| [FeLCl]Cl | 3240 | 2940 | 1590 | 420 | 260 | 1700 | 1500 | 1250 | 640 | 1410 | 1090 | 730 |
| [CoLCl]Cl | 3245 | 2940 | 1600 | 430 | 310 | 1710 | 1540 | 1255 | 650 | 1420 | 1070 | 710 |
| [NiLCl]Cl | 3220 | 2800 | 1620 | 420 | 290 | 1720 | 1520 | 1250 | 670 | 1425 | 1100 | 750 |
| [CuLCl]Cl | 3220 | 2900 | 1600 | 460 | 330 | 1730 | 1500 | 1240 | 680 | 1430 | 1090 | 700 |
| [ZnLCl]Cl | 3230 | 2940 | 1600 | 430 | 270 | 1700 | 1500 | 1250 | 660 | 1450 | 1070 | 720 |

However, amide I band is found to be in the region expected for metal free ligand, thus ruling out the coordination through the amide oxygen[30]. The absorption band observed in the region 2800-2940 $cm^{-1}$ corresponds to CH stretching mode. All the complexes show bands around 1400-1450, 1070-1100 and 700-750 $cm^{-1}$ which are[31] consistent with the phenyl ring vibrations. The bands around 420-460 and 260-330 $cm^{-1}$ were assigned to[32] ν(M-N) and ν(M-Cl) respectively.

### 5.1.6 Reflectance Spectra

The reflectance spectrum of the iron(II) complex exhibit four bands expected at their estimated positions at 5900, 8500, 15500 and 18900 $cm^{-1}$ similar to that reported for a five coordinate Fe(II) complex[33]. While the reflectance spectrum of Co(II) complex show bands at 12540, 16500 and 19450 $cm^{-1}$ ascertaining a pentacoordinated system[33] around Co(II) ion. The reflectance spectrum of Ni(II) complex show one band at 11220 $cm^{-1}$, another at 16750 $cm^{-1}$ and a shoulder at ca. 6500 $cm^{-1}$ characteristic of five coordinated[34] Ni(II) complex. However, reflectance spectrum of Cu(II) complex show a broad unresolved band with a maximum around 11075 $cm^{-1}$ and a shoulder at ca. 15340 $cm^{-1}$ which may reasonably be assigned to a typical pentacoordinated Cu(II) complex [35].

However, the electronic spectra of Mn (II), Fe (II), Co (II), Ni (II) and Cu (II) macrocyclic complexes in DMSO exhibits bands **(Table 3),** which corresponds to pseudo-octahedral geometry around these metal ions resulted due to coordination of solvent molecule (DMSO) at vacant sixth coordinating site around each metal ion. All the complexes show a strong intensity band at ~ 30,000 $cm^{-1}$ due to charge transfer transition. The magnetic moment values **(Table 3)** also complement the electronic spectral data.

### 5.1.7 $^1$H NMR Spectrum

$^1$H NMR Spectrum of Zn(II) macrocyclic complex, recorded in $d_6$-DMSO, exhibit a multiplet in the region 8.16-8.22 ppm assignable to[36] amide (CO-NH; 2H) protons. An additional multiplet in the region 2.29-2.50 ppm may be assigned[37] to methylene (N-$(CH_2)_2$-N; 4H) protons of ethylenediamine moiety. A singlet at 8.48 ppm can be assigned to[38] imine (HC=N; 2H) protons. The protons corresponding to phenylene ring of condensed o-aminobenzoic acid gives four multiplets in the region 7.02-7.60 ppm. Multiplets in the region 6.62-6.86 ppm are assignable to phenyl protons of the o-phthalaldehyde moiety. The spectrum does not show any resonance peak corresponding to primary amino (-$NH_2$), carboxylic (-$CO_2H$) or aldehydic (-CHO) functional group protons supporting the contention that the condensation has resulted in the formation of proposed macrocyclic framework.

**Table 3: Magnetic moments (B. M) and electronic spectral data ($cm^{-1}$) of the macrocyclic complexes with their assignments.**

| Complexes | $\mu_{eff}$ B.M | Band position ($cm^{-1}$) | Assignments |
|---|---|---|---|
| [MnL(Y)Cl]Cl | 5.8 | 18,850 | $^6A_1g \rightarrow {}^4T_1g$ |
| | | 22,300 | $^6A_1g \rightarrow {}^4T_2g$ |
| [FeL(Y)Cl]Cl | 5.3 | 11,500 | $^5T_2g \rightarrow {}^5Eg$ |
| [CoL(Y)Cl]Cl | 4.5 | 15,698 | $^4T_1g$ (F) $\rightarrow {}^4A_2g$ (F) |
| | | 20,661 | $^4T_1g$ (F) $\rightarrow {}^4T_1g$ (P) |
| [NiL(Y)Cl]Cl | 3.0 | 11,682 | $^3A_2g$ (F) $\rightarrow {}^3T_1g$ (F) |
| | | 17,513 | $^3A_2g$ (F) $\rightarrow {}^3T_1g$ (P) |
| [CuL(Y)Cl]Cl | 1.8 | 15,313 | $^2B_1g \rightarrow {}^2B_2g$ |
| | | 18,416 | $^2B_1g \rightarrow {}^2Eg$ |

**Y = DMSO**

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